VOL. XXXI 1917

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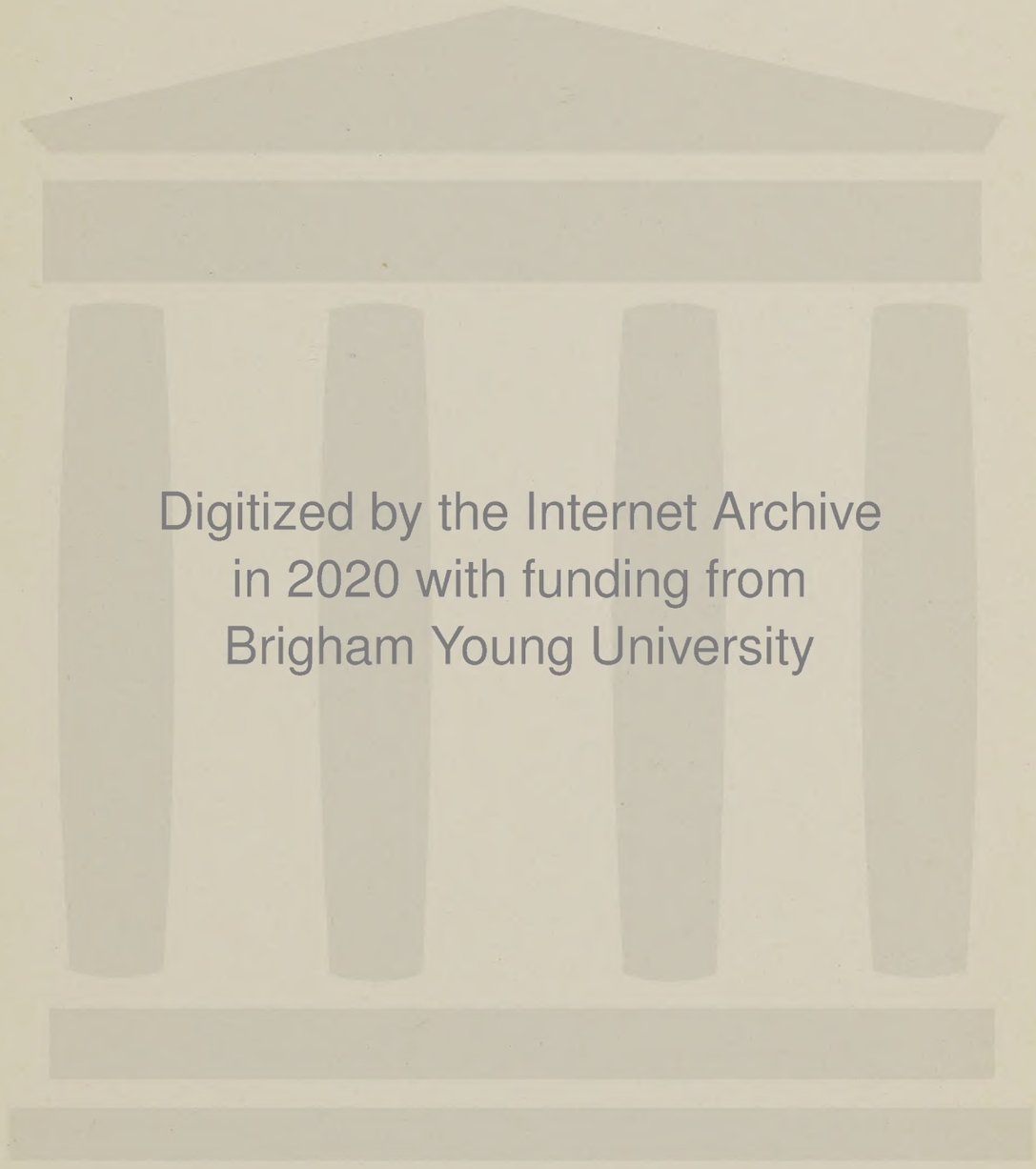

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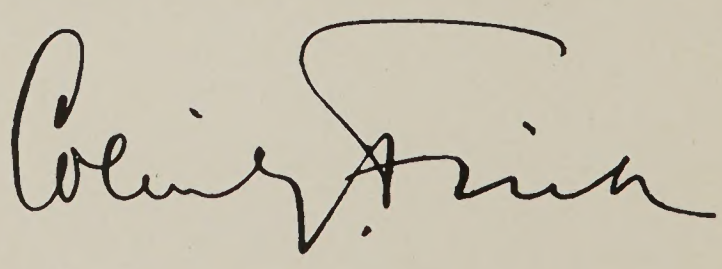

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TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

VOLUME XXXI

157573

THIRTY-FIRST GENERAL MEETING

DETROIT, MICHIGAN, MAY 2, 3, 4 AND 5, 1917

PUBLISHED BY

THE AMERICAN ELECTROCHEMICAL SOCIETY

AT THE OFFICE OF THE SECRETARY

LEHIGH UNIVERSITY, SOUTH BETHLEHEM, PA.

1917

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VOLUME XXXI 1917

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS

CONDENSED MINUTES OF THE THIRTY-FIRST GENERAL MEETING OF THE SOCIETY, HELD IN DETROIT, MICHIGAN, MAY 2, 3, 4 AND 5, 1917.

Number of members registered, 80; number of guests registered, 115; total, 195.

PROCEEDINGS OF WEDNESDAY, MAY 2

The meeting of the Society did not commence until May 3d, but registration commenced Wednesday afternoon, May 2d, at the Hotel Statler, and members and guests left the hotel at 2.00 P. M. for trips to automobile plants. The larger number visited the plant of Dodge Brothers, where they inspected the work, being particularly interested in the electrical japanning ovens, and were later entertained with motion pictures in the company's auditorium. On the evening of this day members and guests, to the number of about eighty, participated in a dinner at "Westwood," where abundant occasion was given the visitors to become personally acquainted with members of the local engineering societies.

After the dinner, the Committee on Public Relations, the Publication Committee, and the Board of Directors, held meetings.

PROCEEDINGS OF THURSDAY, MAY 3

The annual business meeting of the Society was called to order by President FitzGerald in the auditorium of the Hotel Statler at 9.30 A. M.

Secretary Richards read the annual report of the Board of Directors to the Society, accompanied by the annual report of the

Secretary and of the Treasurer. These reports were accepted and are appended to the Proceedings of this meeting.

The Secretary then presented the report of the Publication Committee, which was approved and is appended to the Proceedings of this meeting.

President FitzGerald then read a letter from the Secretary of the Navy, stating that it would be entirely agreeable to him to have the representatives of the Society upon the Naval Consulting Board present to the Society a report on the value of the Board to the Navy and such a statement of the activities of the Board as did not include confidential information.

Secretary Richards then presented on behalf of Mr. Lawrence Addicks and himself, representatives of the Society upon the Naval Consulting Board, a report upon the composition and activities of the Board, which is appended to these Proceedings.

Mr. C. G. Schluederberg, Chairman of the Membership Committee, then detailed briefly the work of his committee during the year, bespeaking the co-operation of all members present in the work of his Committee. The large increase in membership during 1916, as shown in the Secretary's annual report, speaks most elegantly for the work of this Committee. On motion of Mr. Lidbury, seconded by Mr. Fink, a resolution of thanks was passed by the Board, assuring Mr. Schluederberg of its very high appreciation of his excellent service.

President FitzGerald then spoke of the work of the Committee on Public Relations, particularly of the report which it made to the Board of Directors concerning Water Power Legislation. This report was published in the last Bulletin of the Society (May Bulletin), and was presented to the Board of Directors at their meeting last night (May 2d). The Board of Directors, after modifying the report in two places adopted it and voted to present it to the Society for discussion and any action which it might see fit to take. The Secretary then read the modified report as presented by the Board of Directors, calling attention to the two modifications which had been made.

Mr. Lidbury remarked that this report essentially requests that when any pending legislation on water power is under consider-

ation, that the electrochemists of this country be consulted. He then moved the following resolution:

"*Resolved,* That this Society endorses the report of its Board of Directors on Water Power Legislation, and that the report be and is hereby adopted as the report of the American Electrochemical Society."

"*Be it further resolved,* That the report and appendixes be printed, and copies be distributed to the members of the Society at the discretion of the President of the Society."

The motion was passed and the resolution adopted. The full text of the report and its appendixes are printed after these proceedings.

Two amendments to the Constitution, which had been submitted to the Board of Directors, approved by them, printed and sent out to the members of the Society with notice that action will be taken upon them at this meeting, according to the provision of the Constitution, with proxies to allow voting to those who are unable to be present at this meeting, were then brought up for action by the Secretary.

The first amendment relates to Article 4, Section 1, of the Constitution, which deals with the entrance fee. The present Constitution reads as follows: "The entrance fee, payable on notification of election, shall be five dollars. (Charter members shall be exempt from the payment of the entrance fee). If not paid within three months after notification, the election of the applicant is thereby canceled."

The proposed amendment to this section reads as follows:

"The entrance fee, payable on notification of election, shall be five dollars. If not paid within three months after notification, the election of the applicant is thereby canceled. Applicants for membership who are at the date of their election students in attendance at colleges, universities and technical institutions, shall be exempted from payment of the Entrance Fee."

The second amendment deals with the question of a quorum at meetings of the Society. The present Constitution reads as follows:

"A quorum of the Society shall consist of one-tenth the number of members residing in the United States, present in person or by proxy."

The proposed amendment of Article 9, Section 1, reads as follows:

"A quorum of the Society shall consist of fifty members eligible to vote, present in person or by proxy."

Concerning Amendment 1 the Secretary explained, as one of the proposers of the amendment, that being in contact with college students it had been impressed upon him that men who are chemical and metallurgical students are exceedingly promising material for membership in this Society, that all technical societies try to make concessions to these men, to make it easy for them to associate themselves with these societies while still in college, because after leaving, being away from the influence of their Professors, the chances that they will join the proper technical societies are much decreased. If such students can be gotten to join the Society before graduating, many become at once actively interested, frequently organize student sections, and become very promising material for keeping up the membership of the Society. Unfortunately many students are deterred from becoming members because of financial difficulties, and the object of this amendment is to relieve them of the payment of entrance fee, and thus make it as easy as possible for them to join the Society.

It was further brought out in discussion which ensued that the exemption applied to any students enrolled in attendance, whether undergraduate or graduate students; that all such joining the Society become full members, without any distinction whatever from other members of the Society who paid entrance fee.

On the question being called the amendment was passed by the following vote: for the amendment, 31 present and 105 by proxy (votes cast by the Secretary), total, 136; against the amendment, 1 present and 4 by proxy, total, 5. The President declared this amendment to the Constitution carried.

The second amendment being brought up for action, the Secretary explained that the present provision in the Constitution with respect to the number which constitutes a quorum at a meeting of the Society is no longer a working basis, since the membership

became so large that it is impossible to get that proportion of members residing in the United States present at a meeting, except under unusual conditions.

The question being called the amendment was passed by the following vote: in favor, 28 persons and 104 by proxy, total, 132; against the amendment, none of those present, and 5 by proxy, total 5. President FitzGerald announced that the amendment was carried.

The Secretary then read the report of the Tellers of election, which was submitted as follows:

REPORT OF TELLERS OF ELECTION

Following is a list of the votes cast in the election of officers for the year 1917-18:

President: C. G. Fink, 199; W. R. Mott, 1; E. R. Taylor, 1; F. J. Tone, 1.

Vice-Presidents: H. C. Parmelee, 194; F. C. Frary, 164; J. W. Beckman, 99; Edgar F. Smith, 1; C. G. Schluederberg, 1.

Managers: L. E. Saunders, 180; J. A. Mathews, 161; A. T. Hinckley, 129; O. P. Watts, 49; W. R. Mott, 47; H. B. Coho, 39; F. C. Frary, 1; F. G. Cottrell, 1.

Treasurer: P. G. Salom, 200.

Secretary: J. W. Richards, 198; G. A. Roush, 7; R. P. Hommel, 1.

Signed:

BARRY MACNUTT,
G. A. ROUSH,
S. S. SEYFERT.

The President then announced the following elections, as the result of the report of the Tellers:

President: Colin G. Fink.

Vice-Presidents: H. C. Parmelee, F. C. Frary, J. W. Beckman.

Managers: L. E. Saunders, J. A. Mathews, A. T. Hinckley.

Treasurer: P. G. Salom.

Secretary: J. W. Richards.

President FitzGerald then called President-elect Fink to the Chair, while reading his presidential address, as retiring President. The address is printed in full as the first paper in these Transactions.

After the reading of the presidential address, reading of papers and discussions were taken up, as printed in full in these Transactions; *viz.*, paper by J. A. Mathews (abstracted by Secretary Richards), R. F. Flinterman and J. L. Dixon.

The afternoon session was opened at 2.00 P. M. in the auditorium of the Hotel Statler. Papers were presented by the following and discussed as printed in these Transactions: C. A. Buck (abstracted by Secretary Richards), A. A. Meyer, R. G. Williams, L. Johnson (abstracted by Secretary Richards), W. W. Strong (abstracted by Secretary Richards), and C. H. vom Baur.

In the evening members and guests and local friends assembled in the roof garden of the Hotel Tuller for a complimentary smoker, as the guests of Section Q. This unofficial but highly efficient section excelled all previous efforts in the cleverness and brilliancy of its entertainment.

PROCEEDINGS OF FRIDAY, MAY 4

The meeting was called to order by President FitzGerald in the auditorium of the Hotel Statler at 9.30 A. M. Papers were presented by the following and discussed as printed in these Transactions: W. R. Mott, W. C. Moore (abstracted by Secretary Richards), O. L. Kowalke (abstracted by Secretary Richards), E. A. Richardson and L. T. Richardson (abstracted by Secretary Richards), and C. F. Hirshfeld. Because of lengthy discussion, four papers scheduled for this morning's session were adjourned to the Saturday session, for lack of time.

The afternoon was spent in visits, either to the Edison Power House or the electric steel plant of the John Crowley & Co. and the Michigan Steel Castings Company. Every one was highly pleased with the interesting exhibits seen in their visits.

The evening session was omitted, Mr. Alex Dow, President of the Edison Company, being unable to be present. A number of members spent the evening in accompanying the ladies to a theater party.

PROCEEDINGS OF SATURDAY, MAY 5

Reading and discussion of papers was resumed at 9.30 A. M. in the auditorium of the Hotel Statler, President FitzGerald in the Chair. Papers were presented by the following and discussed as printed in these Transactions: W. C. Brooks, M. deK. Thompson, and L. R. Byrne (abstracted by Secretary Richards), W. L. Badger, M. deK. Thompson and T. C. Atchison (abstracted by Secretary Richards), W. E. Koerner (abstracted by C. G. Fink), M. deK. Thompson and O. L. Mahlman (abstracted by Secretary Richards), F. C. Mathers and K. S. Means (presented by Mr. Mathers), F. C. Mathers, K. S. Means and B. F. Richard (presented by Mr. Mathers), F. C. Mathers and L. G. Blue (presented by Mr. Mathers), F. C. Mathers and A. B. Leible (presented by Mr. Mathers), T. B. Briggs, H. L. Pierson and H. S. Bennett (abstracted by Secretary Richards), O. P. Watts and A. Brann (abstracted by O. P. Watts), T. W. Case (abstracted by Secretary Richards).

In discussing W. E. Koerner's paper Mr. W. R. Mott made a motion that a Committee be appointed on Algebraic Signs of Potential and Dr. Carl Hering amended the motion that the Committee be requested to report at the next General Meeting of the Society. The motion was put to vote and carried.

Dr. Carl Hering then presented the following resolution of thanks, which was numerously seconded and passed.

RESOLUTION OF THANKS

The American Electrochemical Society, closing its thirty-first General Meeting, in Detroit, expresses its deep appreciation of the co-operation of the residents of Detroit in furthering the plans for its meeting, and desires to express these thanks in particular to the following:

The Detroit Edison Company, for permission to visit its power plant.

The John Crowley Company, for exhibiting its electric steel furnace plant.

The Michigan Steel Castings Company, for allowing inspection of its electric steel-casting equipment and operation.

Dodge Brothers, for allowing inspection of their works and providing interesting entertainment.

The Packard Company, for the loan of automobiles for use of visiting members and guests.

The management of the Hotel Statler, for use of its fine auditorium for holding our sessions.

The Local Committee of members and friends of the Society, particularly the efficient and genial chairman, Mr. E. L. Crosby, who have given time and effort liberally towards our comfort and entertainment.

The Ladies' Committee for their amiability and hospitality towards the visiting ladies, and to Miss Edna J. Raybould for similar service and also efficient aid in distributing information to members and guests.

To Section Q, whose efforts to relieve the strain of a strenuous day were highly appreciated and set a standard of entertainment provided by this unique, unofficial though welcome Section of the Society.

Retiring President FitzGerald then called President-elect C. G. Fink to the Chair, who, after a few well-chosen remarks as to the future activities of the Society, declared the thirty-first General Meeting adjourned.

REPORT OF THE PUBLICATION COMMITTEE

Since the meeting of this Society in September, 1916, thirty-six papers have been presented to this Committee. Of these twenty-seven papers were accepted and nine rejected. The reasons for rejecting the nine papers were as follows:

Four papers were rejected because they did not deal with subjects relating in any way to electrochemistry.

Four papers were rejected because they did not contain sufficient data or information to make even profitable discussion.

One paper was rejected because it had already been published.

A. T. HINCKLEY, *Chairman.*

REPORT OF THE REPRESENTATIVES OF THE SOCIETY UPON THE NAVAL CONSULTING BOARD

The United States Naval Consulting Board consists of Thomas A. Edison, his assistant M. R. Hutchinson and the following representatives of the several scientific societies named:

American Aeronautical Society—Hudson Maxim, the ordnance and explosive expert; M. B. Sellers of Baltimore.

American Society of Automobile Engineers—H. E. Coffin of Detroit; A. J. Riker of Bridgeport, Conn.

The Inventors' Guild—Peter Cooper Hewitt of New York, and Thomas Robbins of Stamford, Conn., inventor of many mechanical conveying devices.

American Chemical Society—W. R. Whitney, Director of Research Laboratory, General Electric Co.; L. H. Baekeland, inventor of Velox paper and Bakelite (both these are past presidents of the American Electrochemical Society).

American Institute of Electrical Engineers—F. J. Sprague of New York, head of the Sprague Electric Company; B. G. Lamme of Pittsburgh, inventive expert for the Westinghouse Company.

American Institute of Civil Engineers—A. M. Hunt of New York and A. Craven, Chief Engineer of the New York Public Service Commission.

American Society of Mechanical Engineers—W. L. Emmet of Schenectady and Spencer Miller, of the Lidgerwood Manufacturing Co.

American Institute of Mining Engineers—W. L. Saunders of the Ingersoll-Rand Company, and B. B. Thayer of the Anaconda Copper Co.

American Electrochemical Society—J. W. Richards, Secretary of the Society, and L. Addicks, Metallurgical Engineer in the Copper Industry (both these are past presidents of the Society).

American Society of Aeronautic Engineers—E. A. Sperry, inventor of the Giroscopic compass and Bion Arnold, Electrical Engineer.

American Mathematical Society—R. S. Woodward, President of the Carnegie Institute, an eminent astronomer; A. G. Webster, Professor of Physics at Clark University.

The Board has been organized for business as follows:

President: Mr. Edison.

Vice-President: Mr. Hewitt.

Chairman: Mr. Saunders.

Secretary: Mr. Robbins.

Committees: Aeronautics; Aids to Navigation; Chemistry and Physics; Electricity; Food and Sanitation; Fuel and Fuel Handling; Internal Combustion Motors; Life Saving Appliances; Metallurgy; Mines and Torpedoes; Optical Glass; Ordnance and Explosives; Production, Organization, Manufacture and Standardization; Public Works, Yards and Docks; Ship Construction; Steam Engineering and Ship Propulsion; Submarines; Transportation; Wireless and Communications; Special Problems.

The representatives of the American Electrochemical Society, Messrs. Richards and Addicks, are Chairmen of the Committees on Metallurgy and Special Problems, respectively.

The functions of the Board are primarily to receive from the Navy Department such inquiries as to information or advice as may be addressed to it, to refer these to the appropriate committee, and when the committee's report has been discussed and approved by the Board, to report back to the Navy Department. The Board also acts as advisor to the Army Department and to the Council of National Defense, as a Board of Inventions, to examine and advise concerning inventions or ideas which may be referred to it for its opinion, and upon any other matter on which these may wish its advice or assistance.

Besides a mass of small detail which has been passed upon by the Naval Consulting Board, the following instances of its activities may be cited as showing the important influence it is exerting upon the resources and policy of the Navy Department:

The Board advised the Navy Department that it should possess far greater facilities for testing and experimenting, and advised that a Naval Testing and Experimental Laboratory be acquired. Mr. Edison drew up a complete sketch of a laboratory, and the Board urged the immediate necessity for this addition to the resources of the Navy Department. Acting upon this advice, the Secretary of the Navy asked Congress for the necessary appro-

priation, with the result that $1,500,000 has been appropriated to begin the erection of the laboratory.

The Board brought to the attention of the Secretary of the Navy the great danger of our National Defense resulting from the inadequate domestic supply of nitric acid and nitrates, which would, in case of the cessation of importations, limit very seriously our power to produce the large quantities of explosives required in a modern war. The Board advised that immediate provision be made to ensure a domestic supply of nitric acid, adequate for the needs of the government in case of war. Acting upon this advice, the Secretary of the Navy took up the matter actively, with the result that the matter was brought to the attention of Congress, and a bill was passed appropriating $20,000,000 for the purpose of ensuring a domestic supply of nitric acid to the Government such as would be adequate for its requirements in time of war.

The Committee of the Board on Organization and Production, under Chairman Howard E. Coffin, brought forward the question of an industrial census of the United States, for the uses of the Government, which would catalogue the producing capacity of every industry in the country and its facilities for assisting the Government industrially. The advice being cordially approved by the Secretary of the Navy, he called the five largest National scientific societies to its assistance, and organized the following plan of taking the census: The American Society of Civil Engineers, the American Society of Mechanical Engineers, the American Institute of Electrical Engineers, the American Institute of Mining Engineers and the American Chemical Society, were each asked to appoint one member in each State. Thus furnishing in each State an organizing Committee of Five, which would take the census in each State. Each Committee was empowered to call to its assistance any or all of the members of the five societies residing in its State, and delegate to specific, properly qualified men the actual work of visiting specific industries and having the census blank properly filled. In this manner 33,000 technical men were enrolled in the work, and some 25,000 industrial establishments were catalogued and appraised as to the possible industrial or manufacturing assistance which they would render the Govern-

ment. The information was collated and arranged under the auspices of the Consulting Board, and turned over to the Navy Department. The information thus acquired, without a dollar of expense to the Government, has been of invaluable assistance and could probably have been obtained in no other way.

The Committee on Metallurgy has conducted an inquiry as to the improvement in the quality of steel castings for use of the Navy.

The question of improvements in storage batteries was referred to the representatives of the American Electrochemical Society, who asked for assistance from members of the Society.

A special committee on optical glass has been making extensive inquiries into the domestic supply of high quality optical glass. (J. W. Richards, Chairman).

A special committee on "Patents" investigated and reported upon the right and freedom of the Government to use patented inventions.

The Fuel Oil Committee held a conference with representatives of the oil producing industry to discuss questions raised by the Navy Department as to the technique of using oil fuel. The list of questions submitted by the Department was very thoroughly and satisfactorily discussed.

The Committee on Special Problems (Lawrence Addicks, Chairman) was formed when the German Ambassador was dismissed, in order to deal especially with the question of defense against submarines.

A conference to which five naval officers and thirty-five civilians of high standing in physics, electrical engineering and ship construction were invited, was held on March 3d. The problems were divided into (1) optics, (2) sound, (3) electricity and magnetism, (4) nets, (5) ship screens, (6) defeat of torpedoes, and a member of the committee placed in charge of each division. Then a number of associates of the Board were chosen from those who attended the conference, and experimental stations opened for each subject. Fruitful work is now in progress and a "listening station" has been built on the coast where special instruments are being developed. Any suggestions will be welcomed by the Chairman.

In this brief review, the detailed work of many other committees can hardly be mentioned, but in many cases they have obtained invaluable information for the Navy Department.

Although for a year the members of the Board paid all its expenses, Congress appropriated $25,000, in 1916, to pay its necessary expenses, including those of its members in attending meetings.

The Board met monthly, sometimes in Washington and sometimes in New York, until recently, when it has decided to meet twice monthly.

In conclusion, it may be said that the Navy Department is receiving *gratis* the service of a body of experts in considering its technical problems, and through them has the support and assistance of some 50,000 technical and scientific men, who are all anxious to add their little bit towards helping solve the difficult problems confronting the Navy Department.

Jos. W. Richards,
Lawrence Addicks.

WATER POWER LEGISLATION

In legislation affecting water power the American Electrochemical Society wishes to point out why primary consideration should be given to the needs of electrochemical industries.

(1) The electrochemical industries, upon whose products many of the principal industries of the country entirely rely, depend in their turn (with the exception of certain branches such as steel melting, some metal refining, etc.) upon an ample supply of power at prices such as are made possible by hydro-electric generation. (See Appendix A.)

(2) The dependence of general industries on electrochemical products is so great, and the industrial improvement made possible by these products is so far reaching that the use of water power for electrochemical purposes benefits the people as a whole. (See Appendix B.)

(3) Recent advances in steam engineering have brought about a condition in which it is, in most cases, no longer economical to employ water power for purposes which do not utilize the power to its full extent all the time; and considerations of conservation

also demand that power generated from waterfalls be utilized completely all the time, and not intermittently.

(4) Electrochemical industries are able to absorb such power fully and continuously, and only for this class of load, as a rule, is the utilization of water power now economical. Therefore its use in this way benefits the people as a whole far more than does its local use for domestic purposes, street railways and lighting, and other ordinary power purposes. (See Appendix C.)

Most of these electrochemical industries are at present suffering from an extreme shortage of developed water power, and as a consequence they are now unable to supply the urgent demands upon them; a condition which will result in giving to other countries an advantage over the United States in the manufacture of products of vital necessity, in times both of peace and war.

(5) It also appears probable that the time is not far distant when this country must rely on the fixation of atmospheric nitrogen to render it independent of external sources of nitric acid for the manufacture of military explosives, and possibly for the production of fertilizers needed to maintain its food supply. The immediate impediment to the development in the United States of processes already working commercially abroad has been the scarcity of cheap power.

In view of the mutual dependence of the futures respectively of these electrochemical industries and the development of water power in this country, and the great importance of the matter to the nation as a whole, the American Electrochemical Society believes that no legislation affecting water power should be enacted without giving a careful hearing to the electrochemists of the country.

NIAGARA POWER LEGISLATION.

The *immediate* future of a major portion of our electrochemical industries depends on a considerable extension of power generated at Niagara Falls more than upon any other factor. The interests of all—scenic beauty, navigation, and industry—are suffering from the absence of positive action based upon the co-operation of all concerned, both in the United States and Canada. The

American Electrochemical Society believes that it has been sufficiently demonstrated that means can be devised for the utilization of far larger quantities of water power at Niagara Falls than are at present allowed by the treaty, under conditions which will not only maintain the scenic beauty of the Falls, but will at the same time prevent the steady deterioration of the spectacle due to the uncontrolled natural erosion of the Horseshoe Falls and will assist in the improvement of navigation in the upper Niagara and Lake Erie. (See Appendix D.)

The American Electrochemical Society therefore suggests the formation of a joint commission containing representatives from both the United States and Canada of the Government engineers and of organizations interested respectively in the preservation of scenic beauty, in navigation, in electrochemistry, in power development, and so forth, and respectfully requests the administration of the United States Government to take the initial steps towards the organization of such a commission, or to take such other action as may best forward the investigation urged by General Black and endorsed by the Secretary of War. (See Appendix E.)

Appendix A.

As an illustration of the dependence of electrochemical industries on large supplies of hydro-electric power a partial list of materials manufactured in electric furnaces or by electrochemical methods is given below:

Aluminum
Magnesium
Carbon electrodes
Ferro-titanium
Ferro-chromium
Ferro-vanadium
Nitric acid
Carbon bisulphide
Sodium
Carborundum
Caustic soda
Sodium chlorate
Chlorine
Cyanamid
Ferro-silicon
Ferro-molybdenum
Ferro-tungsten
Silicon
Phosphorus
Alundum
Caustic potash
Potassium chlorate
Calcium carbide
Graphite
Electrolytic zinc

In order to produce these materials at a cost which will meet foreign competition, very large amounts of electric energy at low price must be available. Owing to the large demand created by the war and the scarcity of hydro-electric energy various manufacturers have been driven to use costly energy derived from steam plants. Had it not been for the scarcity of hydro-electric energy at low cost the excessive prices of many of the above products would not exist.

Appendix B.

The dependence of general industries on certain electric furnace products is well shown by F. J. Tone in a paper on "Electric Furnace Products" (Trans. Am. Electrochemical Soc. (1916) **29**, 66 *et seq.*) from which the following extracts have been made:

"The manufacture of steel is the greatest of all American industries, and its dependence on Niagara power is strikingly illustrated by a study of the ferro-alloy industry. In 1915 the estimated production of finished steel in the United States was 28,000,000 tons, and in a major portion of this there was employed as the chief deoxidizing agent high-grade electrically-produced ferro-silicon. This alloy is used in practically all steel manufactured by the basic open-hearth process, which in recent years has so far supplanted the Bessemer process as to account for more than 70 percent of the total production. To a lesser extent electrically produced ferro-silicon is used in almost all the other processes of steel manufacturing. * * * A cessation of the supply of ferro-silicon would be nothing short of a calamity to the steel business, and when we further consider that specifications for shell steel for munition purposes call for 0.20 to 0.30 percent silicon, we see the rôle ferro-silicon plays in munition manufacture and the realization of our own program of preparedness.

"The essential element in the manufacture of successful armor-plate and armor-piercing projectiles is introduced into steel by the alloy ferro-chromium. It is strictly an electric furnace product. Without this alloy not a battleship could be provided with protective armor nor a coast-defense gun served with modern projectiles. * * * Considering the metals or alloys of chromium, tungsten, vanadium and molybdenum as a group, it may be positively stated

that in the absence of these products we should not be in a position to build modern battleships, guns, submarines and many other machines necessary for the nation's defense, to proceed with thousands of operations involving the cutting of metals at a rate comparable with the present or necessary to successfully meet foreign competition. A goodly proportion of our steel and metal-working industries, mining operations and scores of other industries would find themselves in the condition of practically twenty years ago. * * *

"The manufacture of aluminum is the largest of the electro-chemical industries in point of power consumed and value of product. Commercial development was made possible by Niagara power, and Niagara Falls was for many years the only seat of the industry. The chief uses of aluminum are in automobile and aeroplane parts, electric transmission lines, cooking utensils, acid containers, the deoxidizing of steel and alumino-thermic welding. Even with the prodigious increase in production the scarcity of aluminum is today very acute and is regarded by automobile engineers as little less than a calamity.

"The electric furnace abrasives, carborundum and alundum, are fundamental elements in the metal-working industries. They have revolutionized the method of finishing metal parts, just as high-speed steel has revolutionized the art of shaping metals by cutting. Artificial abrasives have been gradually displacing natural emery and corundum, until in 1914 they constituted 62 percent of the total abrasives used in the United States. The natural abrasives have practically all been imported, and comprise Turkish and Grecian emery. With the beginning of the war, mining in Greece and Turkey ceased and artificial abrasives have been called on to supply the whole field. There are five plants making artificial abrasives from Niagara power, three of which are on the American and two on the Canadian side of the river.

"The great metal-working industries making agricultural implements, locomotives, cash registers, electrical machinery, fire-arms, flour-milling machinery, paper machines, automobiles and all castings of steel, iron and brass are entirely dependent today for an adequate supply of grinding materials on Niagara power. As a simple example, take the automobile industry. The mechanical perfection of the modern automobile and the interchangeability of

parts have been made possible only by the development of the grinding machine and the grinding wheel. Practically all parts of an automobile are finished with abrasives at some stage of their manufacture. Crankshafts are roughened and finished with grinding wheels, likewise camshafts, pistons, cylinders, and all forgings and castings. It is impossible to produce ball-bearings and roller-bearings without the use of grinding wheels. Cut off the artificial abrasives and force the automobile manufacturer to go back to the grindstone, at the same time eliminating the other products of Niagara power, aluminum, high-speed and special steels, and we would see a works which now produces 500 cars per day reduced to an output of considerably less than 100 cars, with the same force of workmen and the same plant equipment. This would mean such an increase that there would be no automobile industry on its present existing lines.

"Manganese steel, one of the unique materials of engineering, was little known fifteen years ago. Today the output in frogs and switches, burglar-proof safes, dredges, gears and rolls represents many million dollars. No steel tool will cut it. Without grinding wheels to shape and fashion manganese steel, it would still be a metallurgical curiosity. * * *

"Calcium carbide is the material from which is produced calcium cyanamid, the most important compound today in the field of fixation of atmospheric nitrogen, and the source of supply which could be most promptly and positively relied upon to solve the problem of an adequate supply of nitric acid and nitrates employed in munitions of war in the event of a failure of the supply of Chilean nitrate. * * *

"Graphite electrodes are used exclusively as anodes in all electrolytic cells for the production of caustic and chlorine. They are a fundamental requisite of this vast industry. With the supply of platinum cut off they are now replacing this expensive metal as anodes in the electrolytic chlorate processes. Graphite electrodes are extensively used in electric smelting and refining furnaces, producing high-grade steel, alloy-steels, ferro-alloys, copper, zinc and nickel.

"The chief uses of powdered graphite are in dry cells, paints and lubricants. Every one of the millions of flash-light batteries produced in this country contains artificial graphite."

Further evidence of the intimate relation between electrochemical products and the welfare of the country at large is found in paper on "The Chemical Industries," by A. H. Hooker (Transactions, American Electrochemical Society (1916), **29**, 73, *et seq.*)

"It is no flight of fancy to say that our lives and the lives of our families in Niagara Falls, Buffalo and over one thousand other cities, depend on the use of either liquid chlorine or chlorine in the form of 'bleaching powder' or hypochlorite for the sterilization of our water supplies to a point where epidemics of typhoid are avoided. * * *

"Our own army is now using the same chlorine treatment to avoid the dangers from typhoid, which beset our soldiers during the Spanish-American war. In Europe the best preventative of blood poisoning and infection from dirty wounds is reported to be a mixture prepared from 'chloride of lime' or 'bleaching powder.' Without this same 'bleaching powder,' our mills and printing establishments turning out or using book paper and writing paper could not turn out their product; our cotton dresses and sheeting would no longer be white, our shirts and collars from the laundry would be a dirty yellow, and, what is worse, a serious menace to health would result through lack of disinfection. Also, white cotton batting, bleached shellac, chloroform for surgical operations, even the disinfection of our garbage and sinks, call for chlorine in the form of 'Bleach.' This same chlorine is used for the production of carbon tetrachloride, which in the form of 'Pyrene' has become a household necessity as a fire extinguisher.

"To meet the shortage in coal-tar dyes, by the combination of chlorine with coal-tar benzol and toluol, we are now beginning to produce in quantity those necessary 'intermediates' formerly made in Germany, from which are made sulphur black, picric acid, benzoic acid, trinitrotoluol, benzaldehyde or 'oil of bitter almonds,' and dozens of other products of like nature for which we are beginning to feel such urgent need. * * *

"Turning again to the electrolytic products of soda at Niagara we find the production of metallic sodium taking an important place. This forms the basis for the manufacture of the sodium cyanide supply of the country, and without this many of our most important gold and silver mines would be compelled to shut down, to say nothing of the great plants dependent upon the use of

cyanide in electroplating. This same sodium is the basis again for sodium peroxide, used by the analyst as a means of determining fuel values, and as a means of generating oxygen for laboratory use, or in hospitals and in submarines and mine rescue apparatus for preserving the breath of life. It is also used for the manufacture of hydrogen peroxide, used not only for bleaching purposes but also entering so freely into our daily lives as a simple household disinfectant. * * * While yellow phosphorus is no longer used in the manufacture of matches, the sesqui-sulphide is an essential ingredient in the 'strike-anywhere' match, and amorphous phosphorus in the safety match. Whenever you strike a match (not made in Sweden) think of chlorates and phosphorus made by Niagara power, and contemplate the possibility of a general return to the use of the flint and steel of our grandfathers' time, should these industries be expatriated (to Norway for example) for cheap power, and an embargo like the present one exist. Phosphorus also finds an important and irreplaceable use in the metal industry as a deoxidizer and hardener in certain nonferrous alloys, chiefly in the phosphorizing of copper for the manufacture of phosphor bronze used on battleships and for certain bearings on machines, automobiles and some chemical apparatus.

"To sum up it will be seen that a large number of our most important manufactures and products of the utmost importance to the country are directly dependent upon the electrochemical industry. * * * Among these we find the paper mills, soap factories, gold mines, the manufacture of chloroform, disinfectants, matches, explosives and dyes, water purification, cotton finishing, oil purification, and a dozen other activities, which would be seriously hampered or closed entirely without the chemicals electrolytically produced at Niagara. * * *

"We have already noted the fact that some of the coal-tar 'intermediates' so much needed for the manufacture of dyes, explosives and medicinal preparations, are now being made at Niagara Falls. As a rule these products need nitrogen to complete the product —nitric acid or ammonia—and this can be obtained by the fixation of atmospheric nitrogen by means of cheap electric power. The same fixed nitrogen is of equal importance to the agricultural interests of the country. The art is well started, but still in its

infancy, and tremendous advantages to the entire country must ultimately accrue from the solution of the cheap fixation of nitrogen."

Appendix C.

Broadly considered, wasteful and uneconomical methods injure the people as a whole. It is no real advantage to the country at large if purely local interests gain something by the use of uneconomical methods. Therefore a consideration of the conditions under which the generation of electric energy by steam and water, respectively, are economical is necessary in order to determine what is really beneficial. The following extracts throw light on this question. Italics are ours.

"It is natural for a spectator surveying a hydro-electric development to gain the impression that the power comes from the water, which, costing nothing, should render the power cheap. It is evident even to a spectator that outside of bond interest the operating expenses of a water power are relatively very low, being in our typical case only 22.5 percent of the total, which includes ample allowance for depreciation, taxes and insurance. But so much of a dam is in hidden foundations and in parts under water and so much of the long transmission line, rights-of-way and power house and substations is out of view that a spectator, even though liberally inclined towards the deserts of capital constantly underestimates the amount of capital invested and neglects to include in his conception of the cost of the power, adequate charges for the service of the capital.

"Business men know that profits depend not only upon excess of price over cost of product, but on 'turn-over,' which is the ratio of aggregate sales to capital.

"If we compare a steam-electric with a hydro-electric power of the same capacity in both of which the selling price of a horse-power-hour is the same, we must permit out of this selling price a greater proportion of gross profit in the hydro-electric or we cannot yield the same return to capital, since there is three times the capital to be served. In other words, there is only one-third of the 'turn-over.' The activity of capital in a hydro-electric plant is very low, much lower than in a steam station, and much lower than in almost all other branches of industry such as manu-

facturing."—*"The Water Power Situation, including its financial aspect,"* by Gano Dunn *(Proceedings of the American Institute of Electrical Engineers.* (1916) **35**, 586.)

"How can we get power cheaper? Is there any way in which we can develop power cheaper than it is being developed at present, which will admit of the development of the electrochemical processes? If we go back perhaps we will see why the electrochemical industries today are tending to move away from Niagara Falls.

"Fifteen years ago Niagara Falls was unquestionably producing power more cheaply by water than by any other method which could be found in this country. In the meantime the evolution of hydro-electric equipment has gone on quite slowly, as it had a very high initial efficiency. Let us look, on the other hand, at the steam plant. The hydro-electric plant, let us say, has made 10 percent advance in fifteen years, but in capital cost it has not made any advance at all, if anything the capital cost has gone up, as the cost of labor and material has run up.

"Let us look at the steam plant. To begin with, the capital cost of the steam plant in fifteen years has been a little more than cut in two. The next point is that the steam plant is now making power with approximately one-half the coal required fifteen years ago. Those are two enormous points of advantage.

"I was very much interested in going over a situation recently which involved tacking on, as it were, a steam plant to a large hydro-electric system. It fell to my work to look into the economics of the situation as well as the engineering possibilities. *After going into the situation carefully I came to the conclusion that up to a certain load factor we can today produce power more cheaply, with a lower overall cost (including fixed charges and operating cost), by a steam plant than we can by any hydro-electric plant now in existence applied to this particular case.*

"The overall costs of power were approximately equal at a load factor of 60 percent. Above that the hydro-electric plant began to show a little better results than the steam plant. Below that point the steam plant was better relatively as the load factor went down.

"Now what we learn from these facts, is simply this—that if we want to produce power at a lower cost than we can do today by hydro-electric plants, we must use some combination of steam and hydro-electric power, the steam plant for the peak loads and

the *hydro-electric power for that part of the load having load factors of over 60 percent.*"—(Henry G. Stott, *Ibid* (1916) **35**, 1135 *et seq.;* Gano Dunn, *Ibid* (1916) **35**, 1137.)

Appendix D.

UTILITY CONSERVED AND BEAUTY PRESERVED AT NIAGARA.

By John Lyell Harper.

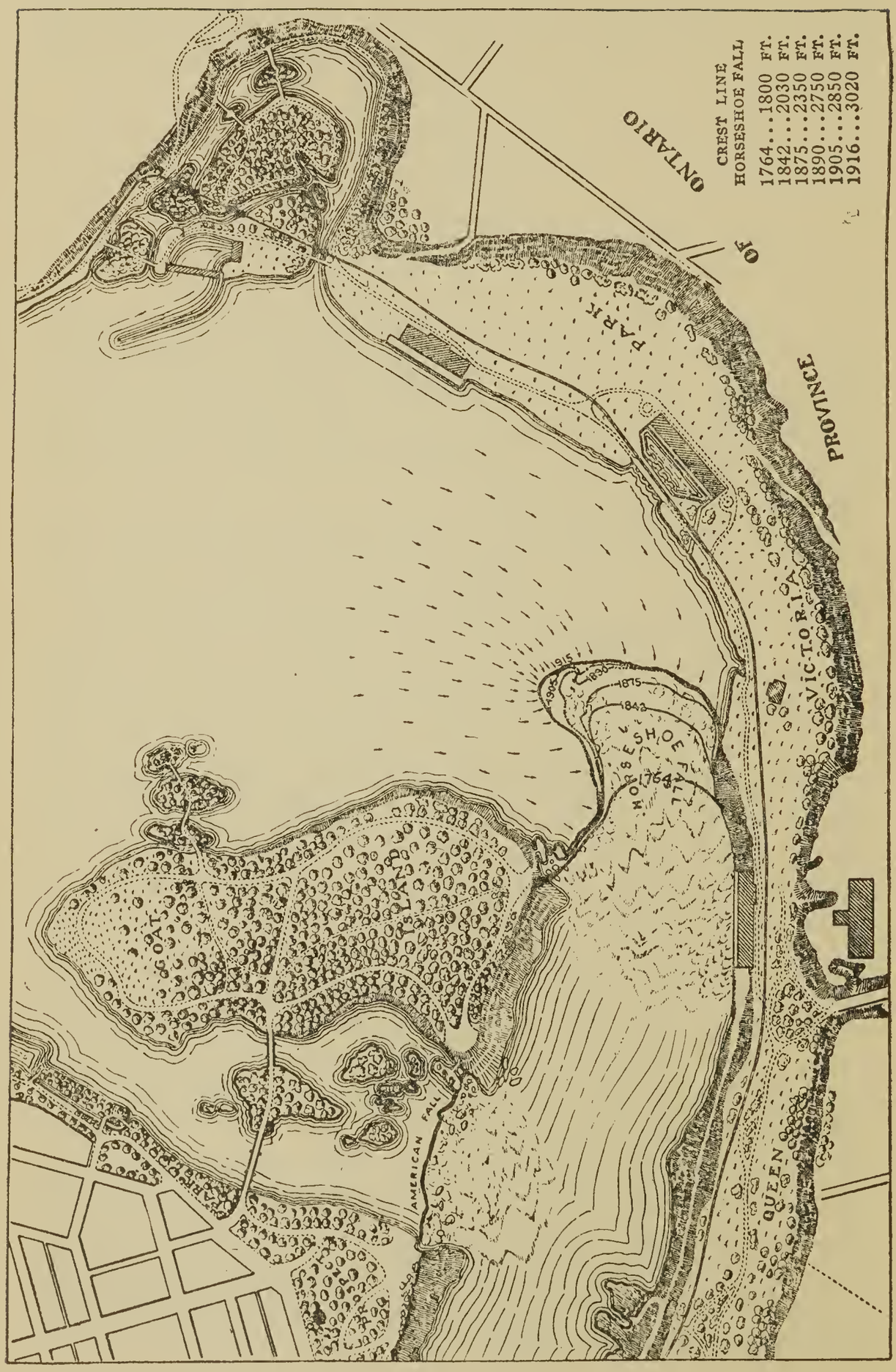
A map of Niagara Falls and the Niagara River has recently been brought to the writer's attention as giving the best illustration possible of the extent and character of the recession of the Horseshoe Fall. This old map was made under the direction of Colonel Bradstreet of the British Army in the year 1764, and is in a fine state of preservation.

The map accompanying this article gives the location of the crest of the Fall in 1764, together with the locations of the crest at later dates, and shows at a glance the conditions obtaining.

The change in appearance of the Horseshoe Fall has always been noticeable within the span of an ordinary lifetime, but passed without serious concern until the subject was taken up by those who imputed this change to the diversion of water for power purposes, though it would seem obvious that, with the lengthening of the crest of the cataract, even an undiminished volume of water would not cover it as deeply as when it was shorter.

Noting the location and character of the recessions shown on the accompanying map, which have been at the average rate of six feet per year for one hundred and fifty years, it may be easily determined that the depletion of the cataract on the sides of the Horseshoe is due almost entirely to the cumulative effect of a constantly increasing volume of water in the center of the river, causing a constantly increasing recession at that point and a more rapid deepening of the river there.

As early as 1908, when Government engineers were making an investigation to determine the effect upon scenic grandeur of a diversion of water from the river, a report was made by Major Charles Keller to the Chief of Engineers of the United States Army, and incorporated in Senate Document No. 105, 62d Congress, which states as follows:


CREST LINE
HORSESHOE FALL
1764...1800 FT.
1842...2030 FT.
1875...2350 FT.
1890...2750 FT.
1905...2850 FT.
1916...3020 FT.
ONTARIO
PARK
PROVINCE
VICTORIA
QUEEN
1915
1905
1890
1875
1842
1764
HORSESHOE FALL
AMERICAN FALL

"While the preceding conclusion as to the effect produced upon the Falls by existing diversion is a statement of opinion based upon ascertained facts, the interests of justice seem to demand the further statement that, in my opinion, the damage already done, and that which may be anticipated from further diversions and from the impending fall in the level of Lake Erie, may be largely, if not entirely, remedied by a submerged dam placed in the bed of the river immediately above the Horseshoe Fall. The dam, if properly planned, would serve to change the direction of the flow so as to increase the streams that feed the Falls at Terrapin Point and at the Canadian shore. The decrease in the mighty volume that overflows the center of the apex of the Horseshoe would not be noticeable. * * * A very direct result of the construction of this submerged dam would be a diminution in the rate of recession of the apex of the Horseshoe. This in itself is extremely desirable."

It is not probable that Major Keller at that time assumed to determine the only way of accomplishing the result, but it is apparent from his report that the fact could have been placed then fully before Congress if a complete investigation and report had been required of him.

Another report made in September, 1911, by Lieutenant Colonel C. S. Riché, of the United States Lake Survey Office, states as follows:

"A large part of the water descending the Horseshoe Fall passes over the center or apex. The recession of this portion of the crest line, due to the enormous flow, is progressing at a rate of about 5 feet per year. In turn, the overflow is becoming more concentrated, and the depths on other portions of the crest are necessarily being decreased. Gauge relations indicate that the surplus over the apex is drawn principally from the Canadian shore. Since 1906 the effect has been a lowering, at mean stages, of one-half foot over the west end of the Fall."

An entire cessation of diversions from the river would not retard the recession of the Horseshoe, but would rather accelerate it. In fact, no negative action by the Government will accomplish a remedy, but a positive action must be taken to accomplish permanent scenic grandeur.

Niagara Falls, "Bone Dry," and with a total water diversion for power purposes is, of course, an interesting picture drawn as a reason for opposing any commercial development, but to those whose lives and energies are daily in contact with the mighty cataract, it represents as unattainable a limit in one direction as does the entire absence of development a wasteful limit in the other direction.

Any observer of the Niagara River during the winter season when almost its entire surface is covered with masses of floating ice will appreciate that a large percentage of the outflow of the river must be reserved, either joyfully or grudgingly as the case may be, for the disposal of this ice. Otherwise, if allowed to stop it would gorge the river all the way to Lake Erie, shutting off the water until it was melted by the heat of the sun in the spring. An estimate of 40 percent of the volume of the river for ice transportation seems to be reasonable; therefore, under the maximum proper development, this 40 percent of the total amount of water would be continuously available for the production of scenic effects.

It may be interesting to consider what can be done with it.

The American Fall, with its 1,000 feet of crest, now discharges about 5 percent of the volume of the river, and, in the opinion of many, produces at least 25 percent of the spectacle. This Fall would be maintained in the same condition as it is at present. Then 35 percent of the river could be discharged over the 3,000 feet of crest of the Horseshoe Fall, and would make a cataract three times as long and twice as deep as the present American Fall.

The scenic effect of this permanent re-establishment would, undoubtedly, be more pleasing than the present one, where at least 75 percent of the water passes over a part of the crest barely visible to the observer, and is absolutely useless for any purpose, scenic or otherwise.

The particular method of distributing the water evenly over the crest of the Horseshoe Fall cannot be determined with exactitude without full and competent study, but it should be accomplished by means of invisible deflectors of such form that there would be no artificial structures visible to the eye. In other words, a perfect distribution should be the only requirement. The means and methods being left to the engineering representatives of the

Government of the United States and Canada, under the supervision of future present commissions having jurisdiction in these matters.

General Black, in his report to a Congressional Committee under date of January 30, 1917, has amplified the previous statements of Major Keller, and the following paragraph taken from his report gives a very clear outline of conditions.

"In the Falls of Niagara the world has one of its grandest and most majestic national wonders. Also it has there a source of power practically unexcelled in amount and convenience of location. There is no question but that, while the beauty and grandeur should be preserved, the source of power should be utilized to the maximum extent possible. There is thus presented a problem of magnitude, but not one which is unsoluble. Study and care are essential if the best results are to be obtained. In my judgment, piecemeal legislation authorizing piecemeal development is inadvisable. Congress should have before it full information as to what can be done in the way of protecting and compensating construction which will permit the maximum diversion of water from the higher level or levels, and as to how water, thus diverted, can be most fully utilized in the production of power. Though the views of this department have been requested repeatedly as to partial aspects of this question, it has never been authorized to make a full investigation."

The above paragraph shows that Congress has before it very clear and concise statements of fact and it is to be hoped that, from the standpoint of electrochemists, early action may be taken which will allow a continuation of the splendid progress made by our scientists, which has not only filled us with pride but is an absolute necessity to our industrial life.

Appendix E.

The recommendation made by General Black appears in a memorandum by General Black, made at the request of the Secretary of War and covers the views of the War Department on policy concerning legislation in connection with the diversion of water from Niagara River.

The memorandum is dated January 30, 1917, and was printed for the use of the Committee on Foreign Relations in report of

hearings before a subcommittee during the second session of the 64th Congress on the bills S. 7803 and H. R. 20047.

General Black reviews clearly and concisely the whole question of the diversion of water from the Niagara River and closes by recommending an investigation of the entire question. He estimates the cost of such an investigation at about $25,000 and the time required at six to eight months.

ANNUAL REPORT OF THE BOARD OF DIRECTORS

To the Members of the American Electrochemical Society:

We submit herewith the annual reports of the Secretary and Treasurer for the year 1916, with detailed financial statement of receipts and expenditures.

The net increase of membership during the year was 184, reflecting the effective activity of the Chairman of the Membership Committee, Mr. C. G. Schluederberg, and his efficient methods. This net increase should in fact be diminished by an unknown number of foreign members with whom it has been impossible to communicate, and whose names are still carried upon the roll. It is probable, however, that the real increase in membership of the Society has approximated 150 during 1916.

The finances of the Society have given concern to the Directors, because of the greatly increased cost of publications and supplies. The new scale of contributions by members, inaugurated in 1916, has however taken care of the increased expenses in a very satisfactory manner. Without such increased income the Society would have been in a bad way financially, and the wisdom of this re-arrangement has been proved by the course of events.

The following are the more important actions taken by the Board of Directors during 1916:

The Board sent an official letter to the Committee of the House of Representatives approving a bill concerning substituting the centigrade scale of temperature for the Fahrenheit scale.

A Committee of Five was appointed by the Board to consider the present status of the Water Power Development, to investigate the present conditions and report to the Board and the

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Society. The committee consisted of Messrs. Lidbury (chairman), L. Addicks, F. G. Cottrell, J. H. Finney, and F. J. Tone.

The past presidents of the Society, with the President of the Society as Chairman, were constituted an Advisory Committee, to recommend action on Public Affairs to the Board and with such powers as the Board may delegate to it. This committee was named the Committee on Public Relations, and was authorized to inform the working committees of Congress of its appointment, and that it was ready to advise Committees of Congress upon electrochemical questions. It was further ordered that this Committee should consist only of citizens of the United States.

A Committee of Three was appointed to consider necessary or desirable amendments to the Constitution. Messrs. Addicks, chairman, Carl Hering, and L. E. Saunders were appointed upon this Committee.

The Board approved the reports by the Committee on Public Relations upon the Nitrate Situation and upon the Tavenner and Van Dyke bill, pending before the Congress. These reports were printed in the Bulletin of the Society for October, 1916.

The Chairman of the Public Relations Committee was authorized to draft and forward a letter to the Secretary of War urging that favorable action be taken upon the use at Niagara Falls of the full amount of water power allowed by our treaty with Canada.

The Board approved the two proposed amendments to the Constitution, which come before the Society at its spring meeting in 1917.

SECRETARY'S ANNUAL REPORT

To the Board of Directors of the American Electrochemical Society:

GENTLEMEN: In 1916 the Society held two general meetings, one at Washington, D. C., April 27, 28 and 29, 1916, at which the attendance was 117 members and 138 guests, total 255; the second at New York City, September 27, 28, 29 and 30, 1916, at which the attendance was 216 members and 281 guests, total 497. The Transactions of the spring meeting include 37 papers, and those of the fall meeting 16 papers.

In 1916 there were issued and distributed to our members two volumes of the Transactions: Volume XXIX, the Transactions of the meeting in Washington, D. C., April 27, 28 and 29, 1916; Volume XXX, of the New York City meeting, September 27, 28, 29 and 30, 1916. These volumes contained 656 and 400 pages respectively.

The Transactions of the New York City meeting, September 27, 28, 29 and 30, 1916, will be issued about May 1, 1917, and will contain 400 pages.

The edition of Volume XXIX was 1,000 copies, bound in cloth for distribution to our members; 50 extra copies in sheets for distribution in pamphlet form to authors of papers; 250 copies bound in paper, for distribution to the Faraday Society; 250 copies sewed, ready for binding, to be kept in stock. The edition of Volume XXX will be 1,300 copies bound in cloth, for distribution to our members; 50 extra copies in sheets for distribution in pamphlet form to authors of papers; 250 copies bound in paper for distribution to the Faraday Society; 250 copies sewed, ready for binding, to be kept in stock.

The stock of Volumes on hand December 31, 1916, was as follows:

Volume	Bound in Cloth	Bound in Paper	Total
I	128	13	141
II	157	0	157
III	63	0	63
IV	88	233	321
V	41	234	275
VI	145	0	145
VII	57	199	256
VIII	76	321	397
IX	75	315	390
X	81	244	325
XI	73	267	340
XII	65	265	330
XIII	177	0	177
XIV	200	15	215

Volume	Bound in Cloth	Bound in Paper	Total
XV	190	224	414
XVI	191	289	480
XVII	104	521	625
XVIII	138	515	653
XIX	10	531	541
XX	5	535	540
Index	312	68	380
XXI	6	554	560
XXII	11	546	557
XXIII	243	293	536
XXIV	2	556	558
XXV	21	537	558
XXVI	39	547	586
XXVII	70	538	608
XXVIII	43	551	594
XXIX	44	500	544

Condition of the Society in regard to membership in 1916:

Members January 1, 1916		1,357
Elected and qualified as members in 1916		245
		1,602
Resignations in 1916	14	
Deaths in 1916	6	
Dropped for non-payment of dues	41	
	—	61
Members December 31, 1916		1,541

Condition, May 2, 1917.

Members January 1, 1917		1,541
Qualified as members to April 28th	59	
Deaths	2	
Dropped for non-payment of dues	57	
Net increase	—	0
Members, April 28, 1917		1,541

Financial Statement.

RECEIPTS IN 1916.

Cash assets beginning January, 1916, account		$1,204 60
Entrance fees	$1,225 00	
Current dues	5,380 95	
Volumes, 1916	3,237 65	
Back dues	390 23	
Advance dues, 1917	1,085 07	
Volumes, 1917, paid in advance	765 00	
Sale of publications	1,166 96	
Advertisements	79 99	
Interest on bonds and bank account	206 05	
Miscellaneous	41 41	
Sale of extra reprints	34 81	
Subscriptions for Faraday Society Transactions, Vol. XII.	211 50	
		13,824 62
		$15,029 22

EXPENDITURES IN 1916

Secretarial appropriation	$1,500 00	
Office printing	659 10	
Express and postage for volumes	271 00	
Office postage	470 90	
Advance copies postage	458 73	
Faraday postage	24 00	
Office expenses	378 22	
Printing of Vol. XXVIII	1,671 66	
Printing of Vol. XXIX	2,354 10	
Advance copies	1,098 39	
Engraving	131 01	
Extra reprints	115 50	
Storage and insurance	112 15	
Local sections	200 00	
Expenses of meetings	829 30	
Publication Committee	12 42	
Membership Committee	275 22	
Committee on Public Relations	16 05	
Advertisement commission	8 00	
Payment on Faraday Society Transactions, Vol. XI	286 06	
Miscellaneous (Payment in error, returned)	11 40	
		$10,883 21
Cash balance beginning January, 1917, account		4,146 01
		$15,029 22

ASSETS JANUARY 1, 1917.

Cash balance, January 1, 1917:		
On deposit	$4,096 01	
Cash box	50 00	
Bonds held by the Society	3,000 00	
Unpaid 1916 dues, since paid	509 89	
		$7,655 90

Obligations:		
Printing of Volume XXX	2,000 00	
Postage and expressage	150 00	
1917 dues paid in 1916	1,085 07	
Vol. 1917 paid in advance	765 00	
Subscriptions for Faraday Society Transactions	211 50	
		$3,211 57
Present worth, December 31, 1916		$4,444 33
Fixed assets, furniture and fixtures and stationery (including stamped envelopes and stamps)		200 00
Stock of volumes on hand, 12,266 copies		not appraised

TREASURER'S ANNUAL REPORT

FOR THE YEAR ENDING DECEMBER 31, 1916.

Jan. 1, 1916. Cash balance		$1,204 60	
January 1, 1916, to Dec. 31, 1916:			
Receipts		13,824 62	
			$15,029 22
Expenditures, 1916			10,883 21
Balance, December 31, 1916			$4,146 01
Dec. 31, 1916:			
Balance Commonwealth Trust Co		$4,613 02	
Less Checks not in, Nos.			
765	4 71		
766	15 00		
767	31 15		
768	286 06		
769	8 00		
770	100 00		
771	223 75		
772	92 90		
		$761 57	
		$3,851 45	
Dec. 31, 1916. Balance E. P. Wilbur Trust Co		244 56	
Balance in cash drawer		50 00	
			$4,146 01

We have examined the above statement of account and receipts and expenditures for the year 1916 and find the same to be correct.

We also report receipt for $3,000 Philadelphia Electric Gold Trust Certificates in the box of the Society in the Safe Deposit Vaults of the Commonwealth Title Insurance and Trust Company, Philadelphia, Pa.

S. S. SADTLER,
CARL HERING,
Auditors.

MEMBERS AND GUESTS REGISTERED AT THE THIRTY-FIRST GENERAL MEETING

Members.

F. C. Atwood
W. L. Badger
R. O. Bailey
T. F. Baily
S. L. Bear
M. H. Bennett
W. C. Brooks
C. F. Burgess
S. C. Carrier
R. T. Chace
N. K. Chaney
A. D. Cowperthwait
Harold N. Cox
F. Crabtree
E. L. Crosby
C. Dantsizen
A. W. Davison
J. L. Dixon
J. V. N. Dorr
A. C. Downes
C. G. Fink
F. A. J. Fitzgerald
F. C. Frary
G. P. Fuller
R. H. Gaines
A. E. Gibbs
C. B. Gibson
H. W. Gillett
J. B. Glaze
S. L. Goodale
J. H. Goodwin
Carl Hering
A. T. Hinckley
C. F. Hirshfeld
H. K. Hitchcock
R. P. Hommel
G. B. Hogaboom
H. W. Kellogg
B. K. Koering
J. M. Lohr
G. E. Long
F. A. Lidbury
C. F. Lindsay
J. R. MacMillan
C. P. Madsen
A. L. Marsh
F. C. Mathers
D. L. Mathias
J. M. Muir
W. R. Mott
E. E. Niswonger
A. G. Randall
A. G. Reeve
J. W. Richards
H. K. Richardson
E. G. Rippel
C. F. Roeber
C. F. Roth
C. G. Schluederberg
J. L. Schueler
J. A. Seede
Acheson Smith
H. H. Smith
F. N. Speller
R. S. Sperry
F. T. F. Stephenson
H. M. St. John
E. C. Stone
S. Temple
F. J. Tone
O. F. Tower
R. Turnbull
M. Unger
C. H. vom Baur
L. D. Vorce
O. P. Watts
H. E. White
R. H. White
B. Wiley
H. H. Willard
A. M. Williamson
C. A. Winder

Guests.

G. L. Alber, Detroit, Mich.
W. H. Allen, Detroit, Mich.
R. J. Anderson, Cleveland, O.
J. C. Armstrong, Detroit, Mich.
A. N. Barron, Cleveland, O.
F. E. Bartell, Ann Arbor, Mich.
E. B. Biggar, Toronto, Can.
C. E. Boyd, Detroit, Mich.
Prof. E. D. Campbell, Ann Arbor, Mich.
Miss Maud C. Carabin, Detroit, Mich.
R. M. Cemerhill, Detroit, Mich.
Mrs. N. K. Chaney, Cleveland, O.
G. C. Clark, Detroit, Mich.
A. B. Conner, Detroit, Mich.
R. A. Cuder, Cleveland, O.
S. Crocker, Detroit, Mich.
Mrs. E. L. Crosby, Detroit, Mich.
T. E. Crossman, New York
J. M. Darke, Lynn, Mass.
C. N. Dawe, Detroit, Mich.
J. A. Dennison, Mich.
H. DeWitt, Detroit, Mich.
G. H. Doan, Detroit, Mich.
Mr. Dowd, Ann Arbor, Mich.
A. J. Dake, Detroit, Mich.
W. D. Dygert, Detroit, Mich.
Mrs. W. D. Dygert, Detroit, Mich.
A. L. Ferguson, Ann Arbor, Mich.
Mrs. F. A. J. FitzGerald, Niagara Falls, N. Y.
R. F. Flinterman, Detroit, Mich.
T. S. Fuller, Schenectady, N. Y.
A. McK. Gilford, Pittsfield, Mass.
J. Gilmartin, Detroit, Mich.
Mrs. J. H. Goodwin, Fremont, O.
Miss M. Graham, Detroit, Mich.
J. Guinther, Welland, Ont., Can.
H. J. Hammond, Detroit, Mich.

Guests (Continued).

Mrs. C. F. Hirshfeld, Detroit, Mich.
H. J. Hawkins, Detroit, Mich.
Mrs. H. K. Hitchcock, Pittsburgh, Pa.
C. W. Jinnette, Detroit, Mich.
J. Kelleher, Welland, Ont., Can.
Mrs. H. W. Kellogg, Niagara Falls, N. Y.
L. H. Knapp, Schenectady, N. Y.
J. Kreusi, Detroit, Mich.
A. H. Krieger, New York
C. F. Kurtz, Bethlehem, Pa.
H. M. Lane, Detroit, Mich.
Mrs. H. M. Lane, Detroit, Mich.
T. A. Lee, Chicago, Ill.
R. B. Lincoln, Detroit, Mich.
E. R. Little, Detroit, Mich.
W. D. Little, Detroit, Mich.
H. E. Lowe, Detroit, Mich.
T. J. MacKavanagh, Ann Arbor, Mich.
A. D. MacLay, Detroit, Mich.
R. J. Macy, New York.
S. R. Manning, Detroit, Mich.
O. J. Marshick, Detroit, Mich.
L. R. McCleary, Buffalo, N. Y.
E. A. McDonell, Detroit, Mich.
A. G. Melcher, Detroit, Mich.
A. A. Meyer, Detroit, Mich.
F. M. Meyers, Montreal, Can.
H. D. Miles, Buffalo, N. Y.
D. R. Miller, Niagara Falls, N. Y.
Miss Ruth Mott, Cleveland, O.
Mrs. W. R. Mott, Cleveland, O.
J. C. Munn, Chicago, Ill.
Mrs. D. E. Murray, Detroit, Mich.
F. H. Nickle, Saginaw, Mich.
J. D. Noyes, Detroit, Mich.
Mrs. John D. Noyes, Detroit, Mich.
J. W. O'Dea, Detroit, Mich.
S. A. Orth, Detroit, Mich.
A. B. Parfet, Detroit, Mich.
Miss F. I. Phipps, Detroit, Mich.
I. L. Pond, Detroit, Mich.
T. P. Purman, Detroit, Mich.
W. P. Putman, Detroit, Mich.
C. F. Quaintance, Golden, Colo.
G. K. Reel, Detroit, Mich.
P. O. Reynedu, Detroit, Mich.
Mrs. E. G. Ripple, Buffalo, N. Y.
Miss Martha Ripple, Buffalo, N. Y.
C. J. Rottman, E. Pittsburgh, Pa.
E. A. Rykenbon, Ann Arbor, Mich.
Mrs. E. A. Rykenbon, Ann Arbor, Mich.
G. K. Saurwein, Detroit, Mich.
E. W. Seaholm, Detroit, Mich.
W. S. Scott, E. Pittsburgh, Pa.
E. M. Shepard, Jr., Detroit, Mich.
A. C. Shepherd, Cleveland, O.
B. Smith, Detroit, Mich.
J. H. Smith, Milwaukee, Wis.
M. B. Smith, Detroit, Mich.
C. G. Snyder, Pittsburgh, Pa.
S. Sowder, Detroit, Mich.
F. T. F. Stephenson, Detroit, Mich.
J. Sullivan, Detroit, Mich.
Allan C. Thayer, Detroit, Mich.
A. L. Turtchell, Mansfield, O.
F. Von Schlegell, Chicago, Ill.
H. P. Wells, Wyandotte, Mich.
G. P. Walter, Narragansett Pier, R. I.
E. P. West, Detroit, Mich.
S. Westberg, Christiania, Norway.
A. E. Westmore, Detroit, Mich.
B. I. Whiting, New York.
R. G. Williams, Worcester, Mass.
T. B. Wipperman, Detroit, Mich.
J. G. Wood, Indianapolis, Ind.

MEMBERS ELECTED AND QUALIFIED.

Since Last Membership List (January 1st, 1917).

January 3, 1917:
H. A. Bate
O. F. Allen
G. M. Grübnau
R. C. Gosrow

January 10, 1917:
T. W. Case
G. P. Fuller
J. D. Mortimer

January 10—*Continued*
E. G. Nutting
C. E. Williams
Geo. H. Taber, Jr.
J. J. Bajda
John P. Megroot
J. J. Hayes
C. N. Richardson
T. Kao

January 17, 1917:
G. K. Elliott
E. L. Knoedler
H. L. Ward
F. C. Wallower
Carl Dittmar
F. A. Kauffman
A. Jacob
W. D. M. Howard
J. D. Detwiler
H. N. Lyons

Members Elected and Qualified (Continued)

January 25, 1917:
L. G. Lilje

February 7, 1917:
E. C. Stone
M. R. Thompson
W. V. Morse
J. H. Schmidt
J. G. Dietrichson
C. E. Ruby

February 24, 1917:
A. W. Morris
M. J. Brown
R. E. Lowe
L. W. Williams
R. E. Zimmerman
E. B. Caulkins

March 16, 1917:
E. S. Hedstrom
C. W. Beard
S. Miyasaki
A. K. Brumbaugh
Walter Miller
P. H. Drinker
T. J. Porro
S. P. Unzicker

March 19, 1917:
H. Bradshaw
Frank T. Smith
J. A. Dalmeida
John Lea

March 28, 1917:
H. L. Ward
R. H. Bowles
J. von Krogh
Paul Arthur
E. L. Mack
C. J. Yunck

March 30, 1917:
J. C. Treadwell
O. L. Mahlman
Mary R. Andrews

April 19, 1917:
W. R. Vogeler
C. S. Treacy
W. L. Badger
E. A. Lof
R. T. Chace
H. R. Schubert
C. S. Ruffner
W. E. Dodge

April 19—*Continued*
H. W. Flashman
C. A. Mann
G. B. Griffin
W. G. Nagel
W. K. Wilson
F. C. Ryan

April 26, 1917:
E. W. Owens
S. E. Hedden
R. D. Pike
O. E. Servis
S. A. Ionides
C. Dantsizen
F. E. Twining
Clemens Laise
G. F. McMahon
J. E. Toomer
R. H. McMillen
J. F. Nestor

May 15, 1917:
F. E. Bartell
L. W. Oldfield
B. S. Drake
B. Mears
T. E. Wilson
G. S. Merrill
James Kelleher
S. Lubowsky
A. F. Plock
H. R. Hambly
J. S. King

May 25, 1917:
Robt. Suman
P. A. Campbell
J. B. Edwards
G. I. Roberts
C. E. Blasius
D. H. McMurtrie

June 1, 1917:
J. D. Mereen
I. Gotoh
E. B. Criddle
G. G. Burt
J. B. Pierce, Jr.

June 7, 1917:
J. H. Andrews
J. M. A. Stillesen
J. Kaku
L. M. Cargo
C. W. Hazelett
J. B. Wise

June 21, 1917:
Th. Swann
W. H. Metson
G. Jinguji
Wm. Buhl
L. Burgess
M. Stotter
J. Guinther
C. F. Hirshfeld
S. J. Eberwein
G. D. Scholl
A. C. Jones
E. W. Westcott
Ernest Lamoureux

June 28, 1917:
E. M. Anger
R. R. Reid

July 1, 1917:
H. E. Linden
J. R. H. Neal
J. M. Kroyer
J. C. Woodruff
Seb. Raimondo

July 26, 1917:
Wm. Voss
H. A. Morin
G. A. Theurer
J. E. Shields
H. S. McQuaid
H. C. Sicard
E. D. Newkirk
H. Watanabe
D. Schaaf
A. P. Sullivan
A. Paulsson

August 17, 1917:
A. C. Buttfield
R. A. Chasurick, Jr.
A. A. Hank
O. E. Cushman
G. E. Hoeft
Ludwig Rosenstein
W. Y. Westervelt
E. J. Fowler
N. J. Goldsmith
C. G. Snyder
R. L. Comstock
J. C. Eaton
C. A. Crawford
John Grotzinger
L. B. Lytle
R. J. Cook

Presidential Address, delivered at the Thirty-first General Meeting of the American Electrochemical Society, in Detroit, May 3, 1917.

THE COMMITTEE ON PUBLIC RELATIONS.

By F. A. J. FitzGerald.

The last three presidential addresses seem to have established a precedent as to the nature of that discourse which I propose to follow because the precedent is probably a good one and also because the subject happens to be the one to which I have had to give more time than to any other during the past year.

Until Roeber in 1914 discussed "Some Economic and Aesthetic Aspects of Electrochemistry"[1] presidential addresses were usually devoted to more or less technical subjects. In 1915, however, Lidbury chose as his subject, "The American Electrochemical Society and its External Relations"[2], and when Addicks last year spoke on "The Modern Engineer,"[3] he undoubtedly had in mind his idea of the Committee on Public Relations, which he had asked the Board to create. Thus, the more recent presidential addresses have been devoted to the relations of the Electrochemical Society to matters of public interest rather than to strictly technical subjects.

This is certainly a symptom of the growing consciousness of the duty of individuals and their numerous groupings to the democracy to which they belong. This growth has been noticeable for several years and has been enormously stimulated by the great war which is trying out democracy as it has never been tried before. Will it prove in this great trial that a government by the people can be carried on successfully with the maintenance of the principle that the State is made for man and not man for the State? Democracy demands something more than a government to which the governed consent. It should be controlled by the individuals and social groups of which it is composed and should be for what

[1] Trans. Am. Electrochemical Soc. (1914), **25**, 17 *et seq.*
[2] Trans. Am. Electrochemical Soc. (1915), **27**, 15 *et seq.*
[3] Trans. Am. Electrochemical Soc. (1916), **29**, 21 *et seq.*

these consider conduces best to their happiness. In order then that a democracy shall be successful the individuals and social groups must take a paramount interest in governmental problems. We are learning that this is necessary and that its lack is one of democracy's most serious weaknesses. The lesson is being driven home all the more rapidly by the great struggle between democracy and another system of government characterized by a far higher efficiency according to its exponents.

How then can a social group like our Society serve in strengthening that form of government which we consider necessary to preserve the right of Life, Liberty and the pursuits of Happiness?

The creation of the Committee on Public Relations is an attempt to answer this question and the proposed activities of the Committee are indicated in the resolution presented by A. H. Hooker, as follows:

"*Resolved,* That this Society endorses the action of its Board of Directors in appointing the Past-Presidents of the Society under the Chairmanship of the President, as a Committee on Public Relations, and expresses its confidence in that Committee and its ability to represent the Society in giving advice to legislative committees and other bodies."[4]

In seconding the resolution, F. J. Tone said:

"I desire to second this resolution, and in doing so I desire to take the opportunity of saying that technical societies have a great opportunity today to make their opinions and their influence felt on public questions. I hope that this Society will avail itself of this opportunity to the fullest extent.[5]

There appear to be three main classes of subjects in which the Committee on Public Relations should act:

(1) Subjects dealing with public questions which are referred to the Society for action either by members or outsiders.

(2) Subjects on which advice is asked for by the Government.

(3) Subjects of public interest and relating to electrochemistry should be studied by the Committee and steps taken to initiate action on these by the Society or its members.

[4] Trans. Am. Electrochemical Soc. (1916), 29, 10.
[5] *Ibid.*

In the past year subjects in each of these classes have been dealt with by the Committee.

As regards certain questions in the first class which have been submitted to the Society the Committee has advised that no action should be taken, on the ground that these are not related directly to the Society's activities or are not subjects on which the Society's opinion is of exceptional value. A good example of this kind of question was a resolution on the subject of "Preparedness," which was sent to the Society with a request that it should be submitted to the members for action. The Committee decided against taking any action, not because it was opposed in any way to the sentiments expressed; but because this particular resolution covered a question that obviously was one for the public in general to pass on and not for a particular technical society.

It was felt that if the Society passed resolutions on all kinds of public questions that were not particularly related to its activities this would weaken the effect of any resolutions it passed on subjects about which it could offer a really expert opinion.

Incidentally this resolution called attention to the question of expert advice, for in one clause it offered an opinion as to the size of navy which the United States ought to have. Possibly a heterogeneous mass of citizens might find an excuse for offering an opinion as to how big our navy should be, on the ground that this expression was based on the expert advice of those competent to give it; but a society composed of individuals presumably more or less expert in their particular branch of technical work should understand the value of expert opinions and therefore recognize its own limitations.

One of the special weaknesses of democracies is found in their appreciation of expert advice. The expert is not ignored, but he is not appreciated correctly. On the one hand, we find frequent examples of the hired expert whose advice is ignored by his employers, probably because of a perverted democratic instinct which dislikes all submission to authority. In private affairs those who are called on to act as experts could give numerous examples and in public matters do we not continually see the impudent ignoring of expert advice in highly technical matters by Con-

gress? On the other hand, we must admit that your expert is too apt to think that special knowledge in work of one kind entitles him to promulgate *ex cathedra* opinions on subjects about which his utterances are far from authoritative—and he is taken seriously. Thus, while tacitly agreeing with the flippant treatment of expert opinion by our political representatives our democracy is apt to swallow respectfully the opinions of a great mechanical and electrical inventor on the physiological effects of cigarette smoking or the historical and ethical considerations of war by a distinguished ichthyologist.

Under an autocracy there is a truer appreciation of the expert and consequently a much more efficient use of his abilities. His patrons are members of the governing class and hence it is merely necessary to satisfy them in regard to his expert knowledge, a far easier task than that of exciting the attention and winning the confidence of a democracy. True, the democracy has its representatives who attend to matters of government, but the scientific or technical man cannot depend upon these alone for recognition. These representatives are chosen by the people, and before being chosen they must convince their constituents that they are more or less experts in their own line. To expect these representatives to convince their constituents that the scientific or technical men are worthy experts is expecting too much. That is obviously a task which must be undertaken by the scientific and technical men themselves.

There is no matter requiring more careful consideration by the Committee on Public Relations than that of cultivating in a democracy a true appreciation of expert opinion. The difficulty of this task is great, as is shown by the experience of army and naval experts, and indeed all technical men employed by the government. In their case, however, the difficulties are exaggerated on account of their relation to the government, which must inevitably curb their freedom to a certain extent. The learned and technical societies, however, are not handicapped in this manner, and therefore are perfectly free to exert every effort to win the interest and confidence of their fellow citizens.

Besides distinctly constructive activity of this kind the Com-

mittee should remember the necessity of guarding against certain dangers which are likely to be present in democracies. One of these is the development of what might be described as political experts as distinct from expert politicians. The latter is a necessity, the former an injurious nuisance.

We often have occasion to complain of the blunders of our expert politicians, particularly in their treatment of technical matters, and are apt to imagine that could we take their places things would be much better. They would, in fact, be far worse, giving results as might be expected if a politician were to take charge of the running of an electrochemical plant. The electrochemist who tries to undertake political work in relation to electrochemistry will end by being neither a good electrochemist nor a good politician. In politico-electrochemical matters we must remember that we can only play a complementary part to the politicians. The politician is as useful a member of society as the electrochemist and the whole profession need not be condemned because of those who are incompetent. An incompetent electrochemist is not an impossibility.

Finally let us remember that our special activities contribute no mean part to the great mass of scientific and technical work which has done so much for the welfare of humanity, and in so far as this is true we may fairly ask for the admiration of those who, with the virtuous king of Brobdingnag, hold the opinion that "whoever could make two ears of corn, or two blades of grass, to grow upon a spot of ground where only one grew before, would deserve better of mankind, and do more essential service to his country than the whole race of politicians put together."[6] But let us not forget that this wise king when Gulliver told him of certain wonderful machines developed by his race was "struck with horror at the description I had given of those terrible engines and the proposal I had made. He was amazed how so impotent and grovelling an insect as I (these were his expressions) could entertain such inhuman ideas, and in so familiar a manner, as to appear wholly unmoved at all the scenes of blood and desolation which I had painted as the common effects of these destruc-

[6] "Gulliver's Travels," Jonathan Swift.

tive machines, whereof, he said, some evil genius, enemy to mankind, must have been the first contriver."[7]

Let us then remember that no matter what advances we make towards the development of new processes and inventions we are only doing half of our duty and cannot in justice pose as benefactors of humanity, unless we also do our part in seeing to it that the results of our labors are so wisely employed that they will prove to be blessings rather than a curse.

[7] *Ibid.*

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 3, 1917, President FitzGerald in the Chair.

COMMENTS ON THE ELECTRIC STEEL INDUSTRY.

By John A. Mathews, Ph.D., Sc.D.

[*Abstract.*]

A review of the inception of the industry, its early development, and its present achievements. Electric steel using molten charges from an open-hearth furnace can be made of as good quality as from a cold charge. It also saves oxidizable ingredients, such as chromium, which are lost when remelting in open-hearth furnaces. Other advantages are discussed. The present electric steel capacity of the United States is eight times that of the crucible steel production and one-eighth that of Bessemer steel.

It is nearly forty years since Sir William Siemens constructed and patented an electric arc furnace which would melt steel. It is not recorded that he believed this laboratory furnace was the beginning of a new industry. Whether he thought so or not, he very clearly enunciated the reasons why electric furnaces ought to be superior to other furnaces where the product is in contact with the products of combustion of carbonaceous fuel.

The writer quoted these reasons a year ago in a paper presented before the American Iron and Steel Institute,[1] but they will bear repetition. The advantages of electric melting, Siemens states, are:

First: The degree of temperature is theoretically unlimited.

Second: The fusion is effected in a perfectly neutral atmosphere.

Third: The operation can be carried on in a laboratory without much preparation, and under the eye of the operator.

Fourth: The limit of heat practically attainable with the use of ordinary refractory material is very high, because in the elec-

[1] The Electric Furnace in Steel Manufacture.—A. I. & S. I., May, 1916.

tric furnace the fusing material is at a higher temperature than the crucible, whereas in ordinary fusion the temperature of the crucible exceeds that of the material fused within it.

In short, he says that the function of electric melting is to "effect such reactions and decompositions as require for their accomplishment an intense degree of heat, coupled with freedom from such disturbing influences as are inseparable from a furnace worked by the combustion of carbonaceous materials."

The soundness of these conclusions as applicable to commercial conditions have been amply confirmed during the past ten or twelve years. Yet, they appear like the fulfilment of prophecy, for they were overlooked and all but forgotten for twenty or twenty-five years, until there arose a group of engineers and inventors in several European nations during the closing years of the last century who perfected various processes for doing in the mills what Siemens had done in the laboratory.

Their enthusiastic claims and rosy predictions were not received with much interest by the steel men. They were thought to be only the dreams of inventors or the wiles of the promoter. The Canadian Government displayed commendable foresight when it appointed a commission in 1903 to investigate them at first hand in Europe. In their report in 1904, Professor Harbord, the distinguished metallurgical authority, stated:

1. "Steel, equal in all respects to the best Sheffield crucible steel, can be produced, either by the Kjellin, Héroult or Keller processes, at a cost considerably less than the cost of producing high-class crucible steel," and,

2. "At present, structural steel to compete with Siemens or Bessemer steel cannot be economically produced in the electrical furnaces, and such furnaces can be used commercially for the production of only very high-class steel for special purposes."

This opinion of a competent observer was not enough to overcome the conservatism of the crucible steel makers. The venerable crucible process had withstood the competition of Bessemer steel and of, first acid then basic, open-hearth steel, and it was only natural that the new rival should be viewed with distrust, notwithstanding the illuminating report of the Canadian Commission.

The writer was at that time solely interested in the crucible-steel business, and found it very difficult to accept Prof. Harbord's first conclusion except in so far as it applied to the induction type of furnace, in which, at that time, no purification of the charge was attempted, and to make good steel one started with selected raw materials just as in crucible melting. The combination of melting and refining in one operation did not appear promising, and such samples of steel as came to my attention did not tend to change my opinion.

Reflection shows, however, that even the pure materials selected for crucible melting come from pig iron by the Walloon, Lancashire or puddling processes, and the finished product of these processes is notable for containing slag and oxides in large amounts and for a general lack of homogeneity. Why, therefore, should the more uniform liquid product of the open-hearth furnace, produced from the same pig iron, be an undesirable base material for electric furnaces, especially in view of the well-known reducing and deoxidizing conditions of the electric process, along with which goes ability to remove sulphur to a very large degree?

This view was generally accepted ten years or more ago by Dr. Héroult and other metallurgists, and the earliest installations of electric furnaces consisted of an open-hearth furnace for preliminary melting and refining, the liquid steel being transferred to the electric furnace for deoxidation, desulphurizing and for making of additions or adjustment of the desired analysis.

Such an installation was first made in the United States by the Halcomb Steel Company, and is now in its twelfth year of operation. A similar installation was made at the Richard Lindenberg Works in Germany at about the same time. Other plants soon appeared here and abroad, nearly all using the duplex process. In addition to the belief in the metallurgical soundness of the process, there was the further belief that electricity could not be successfully and commercially used to do the first melting, and this was true at the time, but now the lower cost of wholesale power and increased electrical efficiency make cold melting feasible in many localities.

At the May meeting of this Society in 1909, Mr. Paul Girod, the well-known inventor of the "Girod" furnaces and a success-

ful manufacturer of steel and ferro alloys in France, challenged the electric refining idea, and stated that one cannot make steel of crucible quality in the electric furnace starting with a molten charge of open-hearth or Bessemer metal. While no figures were presented in support of his opinion, the author stated that it was based upon actual experience. Mr. Girod's theory of all this was that at the high temperature of melting the solubility of open-hearth and Bessemer steel for metallic oxides, oxides of carbon, nitrogen and hydrogen was greatly increased; in fact, increased to such a degree that it was thereafter impossible to free the steel, wholly, from them in the electric furnace unless the charge were allowed to cool off and solidify, followed by remelting.

Mr. Girod predicted, "that prospects based on this process of refining in the electric furnace of steel previously melted in the Martin or Thomas furnace may meet much disappointment."

After twelve years as pioneers in operating this process in America, we can truthfully say we have suffered no disappointment. Just recently has come to my attention the case of a very difficult Government specification, which has never been successfully met by any other material, and I know that at least two or three firms furnishing material melted in the electric furnace from cold scrap have failed to meet it. It must be admitted, however, that most of the recent electric-furnace installations are intended for cold melting. We have two such installations in operation and two under erection, but this is not because of any difficulties with the duplex method, which will certainly be continued. Having tried the two methods of melting, side by side, for a considerable period we see no reason for accepting Mr. Girod's conclusions. In fact, if electric furnaces of large size, say, from ten tons and upward, are to be a success, we believe it will only be upon the basis of using molten charges. They are not altogether successful as cold melters.

The choice of processes seems to be an economic rather than a metallurgical consideration, and local conditions for each installation must govern the choice, while the final success by either process is a matter of individual skill of operation. Our results with either method fully substantiate Prof. Harbord's conclusions.

The electric furnace has not replaced the crucible furnace or crucible steel; its field has been the "production of very high-class

steel for special purposes," as stated in Harbord's second conclusion. In this capacity, the electric furnace was most timely to meet the demands for just this class of material, which arose simultaneously with the birth of the automobile and aeroplane industries. New requirements for materials of construction came into being along with them, and it is in meeting these requirements that the electric furnace finds its best and greatest application. To these, of late, have been added the requirements for munitions of war. Our own furnaces, so far, have not been used for this class of material.

Sir William Siemens stated very briefly and simply the conditions obtainable in the electric furnace. What are the practical results which follow from such conditions? Why does the electric furnace, with proper handling—I repeat it, with proper handling—produce a superior product for the most severe requirements of automobile, aeroplane and munition manufacture?

First: Experience shows that chemical composition of consecutive heats can be held more closely to a standard than with any other process. This is most noticeable when handling easily oxidizable metals like vanadium, chromium, silicon and manganese.

Second: From the above it is apparent less of these metals will have to be added to ensure a given final minimum, hence there will be less of the oxides of these metals produced in the steel and to be removed from the steel.

Third: The more nearly composition can be controlled, the more certain are likely to be the results of subsequent heat treatments.

Fourth: Electric steel is usually chemically purer than any other steel. Sulphur, especially, is readily removed. There has been considerable written of late to show that the effects of sulphur are not as harmful as generally believed. Be that as it may when the sulphur is uniformly distributed, yet it is obvious that segregation of elements is impossible if they are absent. It also follows, if segregation of sulphur and phosphorus are not to be feared, the percentage of cropping may be reduced and the yield of sound metal increased—a step in the direction of economy and conservation.

Fifth: Low sulphur in electric steel usually means a prior reducing condition favorable to complete deoxidation. This condition is favorable to sound ingots, freedom from blow-holes and seams produced from them. Quiet metal has less tendency to segregate in the mold, as to either metallic or non-metallic elements, and produces steel free from "ghost" lines or laminations.

Sixth: Alloy additions may be made in the furnace itself rather than in the ladle, which increases the chance of thorough assimilation, diffusion and homogeneity.

Seventh: From a combination of the above reasons, it unquestionably results that electric steel is less easily injured by overheating than is the case with other steel. It will stand more heat in the forging or heat-treatment without injury; that is, it has a wider safe heat range. This opinion has the weight of both experimental evidence and practical experience in the hands of competent observers among users.

Eighth: Electric steels are usually freer from slag and non-metallic inclusions than are Bessemer and open-hearth steels.

Ninth: All of the above characteristics make for quality, when quality is the first consideration. The electric furnace possesses an economic value in its adaptability for handling and recovering alloy scrap values. Some alloy scraps do not make desirable additions to open-hearth furnaces or, if made, a large share of the alloy metal is lost in the slag. With the widespread and increasing use of alloy steels it is highly desirable that alloying elements be not lost when contained in the scrap.

These advantages and others follow because, as Siemens observed, the fusion is effected in a perfectly neutral atmosphere," and because a number of distinguished engineers and inventors produced commercial, workable furnaces in which these results could be attained on a large scale.

Electric furnaces, like automobiles and aeroplanes, are of little use without skilled operators. They are not automatic devices which run themselves. Carelessness in their operation will lead to disastrous results. They are not nearly as foolproof as crucible furnaces, which require considerable skill but of a different order from that required for electric melting, assuming that steel of

equal quality is to be produced by either process. In the one case, selected materials are used as the charge and no purification is attempted; in the other case very impure materials may constitute the charge from which well refined and deoxidized metal results if and when the melter is competent to carry on the reactions involved. Just as with the best of automobiles, so with electric furnaces, things sometimes go wrong in spite of careful operation. At such times special skill is required to diagnose the ailment and to effect a cure. It is feared that this consideration was overlooked by many firms installing furnaces during the past few years, for in many instances they were put into plants where formerly no steel making of any kind was done, and electric steel will likely be discredited through no fault of electric furnaces but because of incompetent operation.

The United States has taken the lead in electric-furnace development, after a very slow start in which we seemed to be lagging behind some of the European countries. In our own plant we have grown from 500 K. V. A. to 5,500 K. V. A. of installed capacity for electric melting, while in the U. S. A. there is no less than 150,000 K. V. A. in operation or just being installed. The annual tonnage capacity of the furnaces using this current I estimate to be about 1,250,000 gross tons of ingots and castings. It is impossible to figure this exactly, because some furnaces may operate on either refining or cold melting charges, and, of course, the output is much greater when the former method is used. This infant industry already represents an output about eight times as great as the crucible-steel production and one-eighth that of Bessemer production. These two processes are not declining but are more or less stationary, with wide annual fluctuations.

The electric furnaces are at hand—over a hundred of them in the United States—for making large quantities of the highest grade of steel and alloys to meet the growing demands of the industries requiring special quality. It is too early to expect that the product of all the recent furnaces is up to the standard that may reasonably be expected after adequate experience. Equipped as we are, we must become the leading nation in both quality and quantity of electric steel production, as we now are in crucible, open-hearth and Bessemer steels.

With wise state and national policies affecting hydro-electric developments, we may see a great electric-steel trade develop without impairing our coal reserves. At the same time, we shall conserve alloy materials, recover good steel from low-grade scrap, and produce a maximum yield of especially sound steel from a minimum of raw materials used. If the Government will take an enlightened view of conserving our coal by developing or permitting the development of those great and inexhaustible sources of power—the waterfalls—the electric steel manufacturers will do their bit toward practical conservation. The electric furnace can utilize power, which, once over the falls, is gone forever; reclaim materials, which, in fuel-fired furnaces, are irretrievably lost, and produce from them products necessary to the advancing demands of the arts of peace, as well as to the national defense.

DISCUSSION.

J. L. Dixon[1]: The Sheffield steel maker is very keen on what he calls "body" in the steel and rightly or wrongly he says that the chemical analysis of the steel is of very little value as a guide. Of course, the chemical analysis has to be good, but it does not follow that the steel is good if the analysis is good.

In Sheffield it is generally recognized that the best practice is to take puddled Swedish bar (Lancashire bar) and heat it in contact with charcoal for a week or more until the required amount of carbon has been absorbed by a kind of case-hardening action. This process is called cementing. The cemented bar is then melted in crucibles and poured into ingots. The next best result is obtained by melting a mixture of Swedish pig iron and Swedish puddled bar without cementing. The poorest quality is obtained by melting ordinary Bessemer or open-hearth scrap together with the required quantity of carburizing material.

Accepting the above statements as true, it would appear that the reason for the cemented bars giving the best results, is that any oxidation of the material (and, of course, puddled bar is highly oxidized) is corrected before the material is melted. Furthermore, it would appear that if the steel is under oxidizing con-

[1] Chief Engineer, J. A. Crowley Co., Detroit.

ditions when actually molten that the oxidation becomes of a more deep-seated nature, and that the crucible process is incapable of correcting this deep-seated oxidation. Apparently some theory of the above kind is necessary to explain the Sheffield man's disinclination to believe that the electric furnace process can correct the injury caused to the steel by previous oxidizing process.

C. F. LINDSAY[2]: At the present moment the Imperial Munitions Board is putting up at Toronto what will be, as far as I know, the largest electric steel plant in the world devoted solely to cold melting. They are installing ten 6-ton Heroult furnaces for use with cold charges, which will give about 400 tons per day of electric steel ingots.

J. W. RICHARDS[3]: There is being installed in South Chicago a plant which will consist of two 25-ton Bessemer converters, two open-hearth furnaces of 250 tons' capacity each, and ten electric furnaces of 30 tons' capacity each. The three processes will be used in tandem, that is, the metal will be first blown in the Bessemer converter, then put into the open-hearth furnaces, as a sort of reservoir, and eventually will be transferred, in charges of 30 tons each, to the electric furnaces, for final adjustment of the composition and finishing. This triplex process will have a capacity of 50,000 tons of electric furnace steel per month.

ROBERT TURNBULL[4]: Taking the statement of Prof. Harbord, quoted on page 44, "At present, structural steel to compete with Siemens or Bessemer steel cannot be economically produced in the electrical furnaces, and such furnaces can be used commercially for the production of only very high-class steel for special purposes," that may have been the case when Prof. Harbord made this statement, but today the electric furnace can melt cheaper and better than any class of furnace except the basic open-hearth furnace. This is owing to the cost of the raw material employed in the process. In the acid open-hearth furnace the steel scrap is expensive. Low-phosphorus pig iron is selling at $75 per ton, whereas the cheapest kind of scrap can be used in the electric furnace, and to a great extent more advantageously than in any other furnace. Today the raw material used in the electric fur-

[2] Imperial Munitions Board, Ottawa, Canada.
[3] Professor of Metallurgy, Lehigh University.
[4] Maker of Thury Electrode Regulators, Volta Mfg. Co., Welland, Canada.

nace can be a mixture of half turnings and half heavy metal, and this scrap would cost in the United States about $18 a ton, whereas the mixture for the acid open-hearth would probably cost about $30 a ton.

In Canada we are better off than in the States, because we are getting our scrap at a much lower figure. It is safe to say that today, in Canada, the electric furnace can produce steel $15 to $18 per ton cheaper than the acid open-hearth. That applies to existing conditions, which, I think, will continue for several years to come.

Dr. Mathews says that the first electric furnaces used were not for melting cold scrap, but with the duplex process of open hearth and the electric furnace together. This is true so far as the United States is concerned, but the first electric steel furnaces which were built abroad were all for cold melting. The first one was at LaPraz, France, by Dr. Heroult, and the Keller furnace was also built and operated in France. These were for the cold melting of scrap.

I wish to corroborate Mr. Dixon's statement about the difficulty of bringing the steel back from its oxidized state after it has been taken from the open-hearth furnace. Dr. Heroult's idea was that steel had to be super-oxidized, in order to get impurities, such as phosphorus, down to the desired point. But it is known that phosphorus can be brought down to the point wanted in the presence of carbon. Phosphorus can be refined out with three percent carbon in the melt. It is not necessary to bring down the steel in the open-hearth to about 0.05 of carbon, as formerly, but it is generally brought down to 0.30, and under such conditions the steel is not so highly oxidized, and the operation of the electric furnace has been greatly improved thereby.

J. A. MATHEWS (*Communicated*): In reference to what Mr. Turnbull says, while I know that early experiments were made by cold melting, and, in fact, are reported by the Canadian Commission, they were hardly on a commercial scale, and the first furnaces were not successful cold melters because they were under-powered.

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 3, 1917, President FitzGerald in the Chair.

NOTES ON ELECTRIC STEEL MELTING.

By J. L. Dixon.

[*Abstract.*]

A discussion of the details of construction of the furnace, the electrical factors which must be considered, the thermal considerations which affect the efficiency and the deterioration of the furnace, and the chemical reactions which eliminate sulphur from the steel and deoxidize the bath. The discussion is based on several years' practical experience.

The object of this paper is to discuss and to try to arouse discussion on some of the everyday aspects of electric steel melting. The problems discussed are those concerning the electrical and mechanical design of the furnace and also those appertaining to the operation of the furnace.

Broadly speaking the subject may be separated into the following divisions:

1. Mechanical considerations.
2. Electrical considerations.
3. Thermal considerations.
4. Chemical considerations.

One and 2 may be said to concern the furnace designer, while 3 and 4 belong more properly to the metallurgist or operator of the furnace. It is obvious, however, that the manner in which the subject is divided is purely a matter of choice, and that the various divisions are necessarily overlapping and interlocking.

1. MECHANICAL CONSIDERATIONS.

Considering the electric steel furnace from the mechanical aspect it need hardly be said that the apparatus should be of a good substantial construction and, as in the case of most of the appa-

ratus for use in steel mills and foundries, the strengths of the various parts should be much greater than those resulting from the use of the ordinary factors of safety. The need for extra strengths in the main structural parts of the furnace, owing to the tendency for warping under heat expansion, is obvious. It is also obvious that the moving parts of the furnace mechanism, such as the tilting gear and the electrode-raising gears, should be of rugged design so as to withstand the rough usage and lack of attention they will receive in the average foundry.

As regards these gears, however, there are other considerations in addition to the purely mechanical ones. The design and location of these gears must be such that they are fully protected from any accidental break-out or overflow of liquid metal. With all possible precautions break-outs or overflows will occur and it takes only a few pounds of liquid steel to put a lifting screw or a worm gear out of business. The protection of the electrode-raising gears is generally quite a simple matter, but not so with the tilting gear. In the furnaces whose design the writer is partly responsible for, a type of tilting gear giving excellent results mechanically has been abandoned owing to the danger of the gear being damaged by liquid metal. The danger may be very small, but any improvements in this direction will immediately show almost unexpected benefits, owing to the fact that the furnace operators are relieved of an unnecessary anxiety.

Another essential, perhaps the most important, is to avoid too great intricacy. This remark applies in some measure to all parts of the furnace, but more especially to the parts comprising the electrode contacts and supporting devices. With the best possible design and care the insulating materials will occasionally fail. If the parts are water-cooled a breakdown may result from a failure of the water system, due perhaps to an interruption of the supply. The writer recently had an experience of this, owing to a laborer turning the wrong valve.

Whatever the cause of the breakdown it is certainly unpleasant to have to stand on the roof of a hot furnace and endeavor to remove the broken-down part, either by unbolting or by cutting it away with a hacksaw.

In making a choice between a simple and perhaps rough design and one that is more finished and also more complicated, it must

be borne in mind that the apparatus of simple design will need a little more daily attention, but when it does break down its replacement can be made in as many minutes as will be required in hours by the breakdown of a more complicated mechanism.

Before leaving the mechanical part of this subject the writer would observe that in designing a very large electric furnace requiring a large number of electrodes the difficulties may be overcome by suspending the electrodes from an overhead device quite independent of the shell of the furnace. This will certainly be the most convenient arrangement if the furnace is not tilting but is of the stationary type, as is quite probable with the very large furnaces that will come in the future.

2. ELECTRICAL CONSIDERATIONS.

The first question an electrical engineer asks about an electric furnace is "What is the power factor?" In a well-designed furnace the power factor should be 90 percent or more. The principles to which attention must be paid in designing and locating the bus-bars and other parts that carry the heavy current are so well known that it is not necessary to dwell on these here.

There may be noted, as tending to improved power factor, (1) an increased number of electrodes, more especially if they are all of different polarities, (2) a higher voltage on the electrodes. The question of voltage is discussed by the writer later, from another aspect. Another question of importance to the power-station engineer is that of current fluctuations or overloads. Here again an increased number of electrodes is beneficial, owing to the spreading and averaging effect.

A higher voltage on the electrodes tends to increase the fluctuations, but this may be largely overcome by reactance without seriously lowering the power factor.

It must be admitted that this question of current fluctuations and disturbances is often a very serious one, more especially with furnaces connected to small power stations, and the writer feels justified in saying that some radically new design in automatic controlling apparatus is necessary. The various kinds of apparatus in present use are of excellent workmanship, but in principle they do not go sufficiently to the roots of the trouble.

Take, for example, the case of a three-phase furnace with three upper electrodes. When there is an overload on one of the electrodes, either one or both of the remaining electrodes is also overloaded, even though at that moment they are correctly located relative to the bath of metal. But the fact that they are correctly located is not observed by the automatic controlling apparatus which, acting under the impulse of the increased current, raises these electrodes, so that when the offending electrode is brought to its correct position the unoffending electrodes are carrying currents that are too small. In this way a more or less continuous hunting is set up and partly on account of this the automatic controlling apparatus has to be "damped," which lessens its sensitiveness and ability to deal quickly with any real trouble that may occur.

Without attempting to discuss this question in detail the writer thinks that it should not be beyond the powers of electrical engineers to devise a special arrangement of current transformers and perhaps voltage connections also, which together with a suitable arrangement of solenoids would take care of current regulation almost as well as if the apparatus could, so to speak, actually look into the furnace and pick out for itself the particular electrode or electrodes that need adjustment.

The writer would like to note here that he believes that furnaces with a bottom electrode are more easily controlled than those without, because any fluctuation of current in one of the upper electrodes is partly taken care of by the bottom connection instead of being absorbed entirely by its remaining upper electrodes. In this way the hunting due to what may be called false regulation is to a large extent avoided.

The electrical end of the subject has so far been discussed almost entirely from the point of view of the power station. From the furnace operator's point of view it is important that the apparatus should be the best that can be bought, and should be installed in the safest possible manner.

It is not always easy in a steel foundry where room is limited and valuable to install the apparatus in the best way, but any extra money spent in doing this is a very small item compared with the value of the product of the furnace during a period of one or two months.

3. THERMAL CONSIDERATIONS.

Briefly the problem is to change the energy of the electric current into heat with the greatest efficiency, and in a manner such that the greatest portion of the heat is transferred to the material under treatment.

The writer strongly advocates the highest possible voltage for melting down the charge. Obviously the higher the voltage the smaller may be the electrodes and the higher will be the power factor. With furnaces of ten tons' capacity and upwards, a voltage higher than usual has been found to be absolutely essential, but even in smaller furnaces there are advantages in this respect not directly attributable to the smaller resistance or induction losses.

A low-voltage arc melts the material only in its immediate vicinity and, exaggerating a little for purposes of illustration, it may be said that with a low voltage the electrode melts the material immediately underneath it by contact resistance. In this way its electrodes bore down through the charge and there results a shallow pool of metal which must be greatly superheated so that it will quickly dissolve the metal lying in it and upon it. The superheating of this gradually-increasing pool of metal requires an excess of energy, and also the high temperature of this metal is detrimental to the hearth.

On the other hand, with a high voltage the larger arc causes the electrode to melt the metal not only immediately beneath it but also for some distance around it. In this way there results not a small pool of highly heated metal but a larger pool of metal of more moderate temperature, which is less severe on the furnace hearth.

The ability of the high-voltage furnace to fuse the whole charge more uniformly and without taking a long time to melt down the outside fringes of solid metal resting on the banks leads to a saving in energy.

During the refining period it is essential that the voltage be lowered so that the arc becomes practically buried in the slag. This is especially essential if a white deoxidized slag is obtained, as such a slag is a good heat insulator and reflector and the heat of the long arc will be reflected on to the walls and roof of the furnace.

There has been much discussion as to the value of a lower electrode, and many times it has been confidently asserted that a lower electrode is valueless and also a detriment. With equal confidence the writer asserts that a lower electrode has a distinct value from a thermal point of view. On occasions when he has operated a furnace without a lower electrode he has experienced greater difficulty in maintaining the furnace bottom in good shape and more especially in making high chrome steels has experienced difficulty in dissolving the alloy additions.

The writer has already in this paper claimed advantages for a lower electrode from an electrical point of view.

A word may be said here as to refractory materials. As regards the furnace bottom the writer has always obtained good results from either magnesite or dolomite tamped in with tar.

As regards the walls and roof, every one operating electric furnaces is aware that these receive their greatest punishment at the end of a heat. This no doubt is largely due to the reflecting power of the white slag. In addition to this, however, the writer is inclined to believe that there is some chemical influence very active at that time. As is well known, silica bricks absorb mechanically occluded iron oxide (Fe_3O_4); at the end of the heat when the atmosphere of the furnace is strongly reducing the Fe_3O_4 is reduced to FeO, which at once fluxes with the silica. Perhaps, unlike the writer, some of the members have had an opportunity of trying clay bricks, which should be less sensitive to chemical influences than are silica bricks.

4. CHEMICAL CONSIDERATIONS.

The process of refining steel in a basic-lined electric furnace has been described many times, and with the large number of furnaces now operating the process has become common knowledge.

The acknowledged advantages of a white slag are sometimes attributed to the strongly reducing effects of calcium carbide. The writer is inclined to disagree in this, and to attribute the good results not to the presence of calcium carbide but to the absence of reducible oxides, the presence of the carbide being merely a symptom that the deoxidation is approaching completion. It is obvious that, as a result of chemical equilibrium, if there is no oxide in the slag there can be very little in the metal.

The writer is unaware that the mechanism of the reactions by which sulphur is eliminated has ever been described. He believes the reactions to be somewhat as follows:

$$\text{(a)} \qquad \frac{\text{FeS in metal}}{\text{FeS in slag}} = \text{constant}$$

Disregarding the presence of manganese, the only way in which the amount of sulphur (FeS) in the metal may be adjusted is by some alteration of the proportion of FeS in the slag. An increase or decrease of any other sulphide in the slag will have no direct effect on the amount of sulphur in the metal. This is because any other sulphide, in this case CaS, is insoluble in the metal. In the slag itself the following equilibrium is established:

$$\text{(b)} \qquad \text{CaO} + \text{FeS} \leftrightarrows \text{CaS} + \text{FeO}$$

This may be written as follows:

$$\text{(c)} \qquad \frac{\text{CaO x FeS}}{\text{CaS x FeO}} = \text{constant}$$

From this it follows that any decrease in the FeO in the slag will cause a decrease in the FeS, until when the slag is free from FeO all the sulphur exists as CaS. Referring to equation (a) it follows that when there is no FeS in slag there is no sulphur in the metal. Probably the slag might consist of CaS entirely without affecting the steel in any way.

Something might be said as to the effect of magnesia in the slag. MgO in the slag is generally recognized to be very undesirable. At the best the MgO dilutes the slag and also robs it of fluidity, so that for a given degree of fluidity an increase in the proportion of MgO means a much greater decrease in the proportion of the active constituent, CaO. In addition to this, however, it would appear that MgO is actively harmful, and the writer believes that under the electric arc it acts as an oxidizer.

Several years ago when burning in a magnesite bottom by lowering the electrodes onto a shallow bed of coke, it was found that whenever the arc came near to the magnesite bottom deep chan-

nels were cut in the bottom. It was apparent that the following reaction was going on between the coke and the magnesite.

$$MgO + C = CO + Mg$$

Directly the vapors of CO+Mg got away into the cooler parts of the furnace the reaction was reversed and there was deposited on the walls of the furnace a powder consisting of finely powdered MgO and soot.

Possibly some reaction similar to this goes on between the MgO in the slag and the carbon in the steel and the carbon, such as coke, thrown on to slag for deoxidizing. Also it is possible that MgO reacts with metallic iron, forming Mg which is lost by volatilization and later reoxidation, leaving FeO in the slag.

The writer remembers with painful distinctness several heats in which the carbon could not be moved from about 0.10 percent. Pig iron was added with no effect, about a ton of pig being added to a five-ton charge. No scale or ore had been charged, and the disappearance of the carbon could only be explained by some of the above assumptions as to the action of the magnesia in the slag.

These experiences were of several years ago, and by fettling the hearth of the furnace with good dolomite and making the slag from fairly pure lime, the difficulties were soon overcome.

In conclusion the writer would state that this paper is not submitted as covering the whole subject, or any part of the subject in detail, but merely as a few notes covering several years' experience in electric steel making.

DISCUSSION.

ROBERT TURNBULL[1]: The question of the tilting gear is quite serious. There is no doubt that if metal bursts through the furnace, or escapes through the doors, this gear is likely to be distorted or injured. The U. S. Steel Corporation builds the tilting gear under the furnace, which makes it more serious still, but in the plant which is being installed in Toronto, a roof is being put

[1] Maker of Voltage Regulators, Volta Mfg. Co., Welland, Canada.

over the entire tilting gear, so that any metal escaping from the furnace will either collect on the roof or flow back into the pit.

Another design, which is being applied in small furnaces, is simple and not costly. The furnace is on trunnions, placed about two-thirds from the front, and the tilting is done from the front, like the Wellman open-hearth furnace. The tilting is done by two hydraulic rams, enclosed in brick walls. These rams are lowered to tilt the furnace and raised to return it to its horizontal position. If the tilting gear can be lowered, as is done in Toronto, the danger of the melt getting onto the tilting mechanism will be diminished.

In regard to what Mr. Dixon says about the electrode contacts, supporting devices, etc., for a long time we have been wedded to copper for all of these devices, that is to say, for electrode holders and roof coolers, etc. In such cases we have used copper exclusively, especially for the larger furnaces. Lately, however, we are getting away from it entirely, and I think in the future you will find all electrode holders will be made of cast steel. We have had cast-steel holders in use now for over a year, and we have had absolutely no trouble at all with them. Electrical men would have expected trouble with the cast-steel holder owing to induction losses around the electrode, but that can be gotten over by using a copper bolt instead of steel bolts for tightening up the holder.

Where 25-cycle current is used cast-iron roof coolers are just as good as cast copper. You do not notice any losses at all by induction. For 60-cycles the loss is somewhat greater, and of course they heat up considerably. I would not say that I would put them on 60-cycle furnaces, but anyone who has 25-cycle current can use cast-iron roof coolers with as good results as, and perhaps better than, the copper ones.

Concerning the question of large furnaces being made fixed, instead of tilting, if this can be done (and there is no doubt about it), it would appear that the electrical difficulties which surround the present tilting type will be greatly done away with. We will be able then to go to the fixed type, which is practically the only one used in smelting purposes, for making ferro-silicon, ferro-manganese, or any of these ferro alloys.

We use without any trouble up to 60,000 amperes on these large furnaces, and get a power factor of 94 or 95 percent in the case of the 25-cycle apparatus, and a power factor of 88 or 90 percent in the case of the 60-cycle apparatus. That is owing to the fact that all steel work is kept away from the conductor bars.

I do not know whether in the case of using an acid hearth electric it is necessary to remove the slag. If it is not necessary, when using the duplex process of combined basic and acid electric furnaces, then a fixed furnace might be used as an acid open-hearth furnace.

Concerning electrode regulation, I think I can speak for our competitors as well as ourselves, by saying there is not enough co-operation between the steel-furnace man and the manufacturers of regulators. We have to supply regulators without knowing sometimes under what conditions they are going to be used. We often do not know what kind of motor is going to be used, whether high- or low-speed regulation, or the kind of winch that is to be employed. Some winches are most difficult to regulate, whereas others turn so easily, if a large motor is put on, that it becomes very hard to regulate the furnace. If there was more co-operation with the steel-furnace man, and if he would not interfere, as he sometimes does, with the man who is making the regulator, I think we could produce a regulator that would completely satisfy him.

In some cases we supply the regulators for standard furnaces, knowing what conditions we have to meet, and we get pretty good results in those cases. In other cases we do not know what conditions have to be met, the regulator is shipped, is installed by the customer, started by him, and if it does not give satisfaction the whole blame is put on the regulator.

I suggest that the makers of electric furnaces should get together with the regulator manufacturers, tell them their troubles (we know some of these troubles but not all of them) and thus it would be possible for us to find remedies and to supply a regulator that would be satisfactory to the customer. If the users, on the other hand, alter the regulators without consulting us, we can not be expected to take the same interest or responsibility as in the case of a mutual study of the question. All we

ask is that we be free to make any improvements which might overcome the difficulties complained of in the regulators, and if they are satisfactory that the customer will continue to do business with us.

Mr. Dixon points out that present-day regulators are not capable of taking care of all the points of necessary regulation, that they ought to be able in a sense to think, thereby combining the automatic and human elements in the regulation. When the automatic regulator was brought out, the human or hand regulation was dispensed with, and electric furnace work was greatly improved. From what Mr. Dixon says, the problem is to produce an automatic human regulator which would meet all requirements in the regulation of a furnace, acting both as a human mind and as a machine at the same time. I would suggest that if the furnace be controlled both by voltage and current, or, in other words, by watts, some of the troubles mentioned by Mr. Dixon would thereby be eliminated, the regulator would be slightly more complicated, would cost more, but better regulation would be ensured.

I will suggest that the makers of steel furnaces and the makers of regulators get together, and take up the different points which arise in automatic regulation. The regulator manufacturers could then work out the problems, and it is safe to say that the electric furnace men would be better advised to leave this work to the regulator manufacturer, than to try to correct such troubles themselves, as they sometimes try to do, with the hammer and chisel.

I have one thing to say concerning the evident difficulty of getting carbon into steel, when magnesia is present in the slag. Whether the reaction given by Mr. Dixon is really what is happening in the furnace, I cannot say, but there is no doubt about it, when magnesia gets into the basic slag, carbon is difficult to introduce into the steel, for some reason or other. The carbon disappears, but where it goes I cannot say. When a basic bottom comes up the best thing to do is to tilt the furnace and take out the slag; because if you try to use the slag with magnesia in it, you are increasing the duration of your heat three to four times, and the resultant metal will be poor. I can certainly corroborate Mr. Dixon in that respect.

J. A. SEEDE[2]: An automatic regulator for the ordinary electric furnace has a difficult task in controlling the position of a heavy piece of machinery weighing a good many hundred pounds, within a small fraction of an inch, and I think the results at present obtained are excellent.

The average load curve of an electric furnace is so much better than the load of an ordinary motor that it is difficult to understand how the central station can make a protest.

Mr. Dixon has pointed out that the power factor in a well-designed electric furnace equipment should be 90 percent or better. As this figure is approximately 10 percent better than the average induction-motor load, it looks as though there was some discrimination against the electric furnace. It is always a matter of concern when high power factors are discussed in connection with electric furnaces, as a power factor of 95 or 96 percent brings you to a condition that will cause any control equipment to keep the electrodes moving up and down, with resultant hunting.

Mr. Dixon apparently believes that it will be a simple matter to design control equipment that will compensate for an overload on one electrode when part of the current is divided among other electrodes. If a demand exists for such a refinement, a solution will undoubtedly be found in a short time.

Mr. Turnbull has spoken about the use of cast-steel electrode holders, and I would like to ask if they are being used on large furnaces, such as 6-ton capacity, or are they used only on small furnaces? Mr. Quinn has been using steel holders on a 1-ton furnace, and it would be interesting to know to what furnace capacities their use can be extended.

ROBERT TURNBULL: I will say, in reply to Mr. Seede, that the holders we have been using are for 17-inch (43 cm.) electrodes, and this applies to the six-ton furnace.

E. C. STONE[3]: The reason that the central station objects to the current fluctuations in the electric furnace is not so much the percentage fluctuation as the fact that the ordinary furnace is very much larger than the ordinary motor. For instance, we

[2] Electrical Engineer, General Electric Company, Schenectady.
[3] System Operator, Duquesne Light Co., Pittsburgh.

have to handle 1,000, 2,000, 3,000 or possibly 4,000-kilowatt units on the electric furnace, and we have very few motors that handle 3,000 kilowatts. I am speaking of a system which has a demand of about 90,000 kilowatts. We have a number of electric furnaces on our lines, and we find in every case that it is necessary for us to completely isolate the electric furnace installation from the rest of the system. That, of course, leads to a certain amount of additional expense, and must necessarily raise the cost of power to the furnace man. A method of regulation, if practicable, which would keep the fluctuations within bounds, so that the electric furnace load could be put right in with the rest of the service and handled on the same transmission lines, and by the same transformer, would unquestionably lower the cost of the service.

While every electric furnace installation we have has to be practically isolated, we have only two motor installations which are sufficiently large to require this same isolation, because the average size of the motor unit is so much smaller than the average size of the furnace unit.

Another point of interest to the central station man is the raising of his load factor, that is, equalizing the load during the twenty-four-hour period. Everything that the electric furnace operator can do, either to regulate his demands to fit in with the central station demands, which are not flexible and cannot be changed, or to entirely shut down during the central station peak period, will, of course, be advantageous to the central station in enabling it to operate at a higher load factor, and must inevitably result in reducing the cost of power. The electric furnace load, provided the schedule of operation is adjusted to fit in with the central station's existing load, will be bound to have a tendency toward reducing the cost of power, and therefore will be a mutual advantage to the furnace man and the central station.

JOHN A. SEEDE: I would like to have Mr. Stone tell us the worst overload he finds on average furnace conditions. Taking, for instance, a 1,200-KVA bank, does he find that the overload is 2,400 KVA, and, if not, what is the relation between the maximum and the average overload?

E. C. STONE: I am afraid I cannot give very satisfactory figures on that. In making some measurements, we found that the average load factor of some of our furnace installations was about 35 percent; that is to say, the ratio of the average consumption per hour to the maximum consumption per hour, over a week's period, was only 35 percent. But, on the other hand, it appears that occasionally the electric furnace will be very nearly short-circuited, and judging by our load fluctuations there must be swings of at least five or six times normal load of the furnace. I am not absolutely familiar with the method of regulation that is used in these installations in Pittsburgh; they have been put in within the last eighteen months, and I presume that they have thoroughly up-to-date regulating methods. I think big swings of five or six times normal load would be a fairly good estimate.

J. A. SEEDE: I would like to discuss Mr. Stone's remarks for a moment. I do not know how he obtained this ratio of the overload being five or six times the normal load, but with a standard 6-ton furnace taking 1,200 KVA at 90 percent power factor, on a 60-cycle circuit, the reactance will be about 43 percent. A short circuit on all three phases in such a furnace, a condition that is very infrequent on account of the regulators and the high contact resistance of the cold charge, would give a maximum current of approximately 230 percent of the full load current.

E. C. STONE: I have no actual measurements of the currents in the furnace, but judging from the voltage fluctuations at certain points, it is quite possible I put the figure too high. It is, however, absolutely correct to say that these installations have to be practically isolated from a load which requires any very good voltage regulation. I would like to ask, for the information of the central station companies, what voltage regulation would be considered absolutely satisfactory for electric furnace work? We were under the impression, until quite recently, that as far as voltage was concerned, the electric furnace was rather crude, and could take almost anything we were willing to give it; but we are learning differently now, and it looks very much as if we would have to give fully as good voltage regulation to the furnace man as to our most particular customer, and perhaps

better voltage regulation than to the average customer. I would like very much to get a figure on what standards we ought to work to in voltage regulation, by which I mean the relation at the high-tension side of the transformer between the highest voltage and the lowest voltage for practical operation.

J. A. SEEDE: It is difficult to make a definite statement in regard to voltage regulation, but one case might be cited to indicate excessive variations that exist in certain localities. I was visiting a small plant where trouble had been caused by low and varying voltage, and found that on one occasion serious difficulties had been experienced by the voltage dropping from a normal value of 220 to 145. Such a condition might easily result in serious accidents, and everything should be done to remove such possibilities.

J. L. DIXON: In reply to Mr. Turnbull's remarks on regulators, where he intimated that we had not supplied the regulator makers with enough information, and had not pointed out any of the difficulties, I think most of the regulator makers have seen as many electric furnaces at work as I have, and I think it is the duty of the furnace maker only to give ratios on the gearing, so that the regulator man can work out the right speed of the motor, and the right ratio of his transformers, in order to give the correct speed to the electrodes. If any further complications are necessary, the electric furnace man must take care of them.

Regarding voltage regulation, I think it is advisable in every case to have the transformers made with extra taps, giving ten percent above and ten percent below normal voltage, in order to take care of any variation there is on the lines. Of course, that will not take care of any variation during the day's run; you cannot avoid that, but it is my thought that it is important, in furnace work, to maintain the voltage somewhere near constant, as a variation of even ten percent will materially affect the working of the furnace.

Regarding the suggestion for steel holders and iron cooling rings, I think the iron cooling rings more especially are a great improvement. Should the cooling rings burn out from the defective water supply, not only is the lost casting of less value in the case of an iron ring but there must also be considered that

in the case of a bronze ring there is contamination of say a 6-ton charge of steel with about 100 pounds of copper which is not good.

I think the suggestion for separate lines direct from the sub-station with no other customers on the line is good. It often happens that the demands of a furnace customer will absorb the full capacity of one line, in the future, and therefore for that reason alone it is not desirable to add any more customers.

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 3, 1917, President FitzGerald in the Chair.

THE ELECTRIC FURNACE IN THE STEEL CASTING PLANT.

By R. F. Flinterman.[1]

[*Abstract.*]

The author discusses castings used for automobile trucks and light machinery parts where the lightness of section precludes manufacture in open-hearth foundries. Such castings run from one-half lb. (0.25 kg.) to 300 lb. (140 kg.); average weight about 20 lb. (0.9 kg.). The author discusses the manufacture of such castings by the crucible process, side-blown Tropenas converter, and, finally, the electric furnace. Two Heroult furnaces are used by the Michigan Steel Castings Company, one of six-ton capacity and the other three tons. Adaptation to shop conditions has been entirely satisfactory, and the furnaces have come up to all expectations. The quality of the electric steel, both the basic and the acid, has proved superior to the converter metal. The author describes the operation in his electric furnace at length, giving composition and mechanical properties of the castings obtained, and discusses the reasons, from his point of view, for the superior quality of the steel thus produced. Finally, the author proposes an improved method of "reversed duplexing," by which the electric steel would be first made in a basic furnace and finished in an acid furnace, thus obtaining the distinct advantages of both kinds of furnace lining.

Under the term "small steel castings" is meant castings, used for the most part for automobile trucks, tractors, light machinery parts, and for other purposes, where the size and shape of the part, its lightness of section and difficulty of production preclude its being made practically in open-hearth foundries. In the latter the work is largely a tonnage proposition. The work is much

[1] President, Michigan Steel Castings Co., Detroit.

heavier and on the whole simpler, and the methods used cannot be applied successfully to the manufacture of lighter and more intricate castings.

The castings we have been manufacturing will run from ½ lb. up to 250 or 300 lb. (0.23 kg. up to 113 or 136 kg.). We do make some pieces running up to 2,000 lb. (910 kg.), but the average weight is about 20 lb. (9 kg.).

We have started with this preface so that our discussion of the methods we have used for the production of castings may be understood to apply to this class of castings only.

Before proceeding to the electric furnace it may be well to touch briefly upon the processes we used before installing the electric furnaces, and also our reason for changing.

Our first method was the crucible furnace. This was chosen because of the low first cost of installation and also because of the generally accepted fact that crucible castings were of very high quality.

The great difficulty with the crucible process was in the crucibles themselves. The crucibles lacked uniformity and were expensive. An average of three heats was considered good and at that rate meant about one cent added to the metal cost. Many crucibles would not come up to this average, and in order to save them as much as possible the final addition of ferro-silicon and ferro-manganese were cut down to a minimum. The result was a steel of low manganese contents, about 0.40 percent, and as a consequence a steel which was not always deoxidized. The inability to keep the carbon low, because of the absorption of carbon from the crucible was an added aggravation.

Our second method was the side-blown Tropenas converter. The advantages of this method over the crucible process might be stated as follows:

1. The process enabled us to make larger quantities of metal at one time. We used converters of one-ton capacity and two-ton capacity.

2. Our metal was uniformly hot and fluid and of fairly regular analysis.

3. We were able to increase our manganese content and consequently were getting very much better results on physical tests.

4. Our metal cost was much reduced. This was a distinct advantage, particularly since the cost varied little from month to month, while in the crucible process our cost depended entirely upon crucible performance, over which we had no control.

Our third and very likely our final choice of method was the electric furnace.

The question of an electric furnace had had our attention for a number of years. The various types and their development were carefully followed, and we finally decided upon the Heroult electric type, installing our first furnace of 6-ton capacity in November, 1915. Our second furnace, of 3-ton capacity, was ready to be run February 12, 1916. Both furnaces have been running continuously since their installation and our converters have been discarded.

Like any new installation, it required several months to adapt same to our shop conditions. This has, however, long since been accomplished and the furnaces have come up to our expectations most completely.

As regards the quality of the electric steel, there is no question of its superiority over the converter metal. This applies to both acid and basic electric steel.

It is only natural that this should be so, if you compare the two methods. In the converter at the end of blow there is a mass of metal at a high temperature, covered by a highly oxidized slag and the metal itself undoubtedly containing oxides. The addition of ferro-silicon and ferro-manganese at this point deoxidizes the metal more or less completely, but the metal is still in contact with a slag carrying a high percentage of iron oxides, etc.

In the electric furnace the covering slag is completely deoxidized before ferro-silicon and ferro-manganese final additions are made. The metal is constantly giving up oxides to the slag during the deoxidizing period and is practically free from oxides before the final deoxidizers are added.

In our opinion it is the more complete absence of oxides in the electric steel, which accounts for the superiority of this steel over converter steel. The results obtained on physical tests are universally better.

The following results are typical:

No.	Maximum Strength		Elastic Limit		% Reduction in area	% Elongation in 2"
	lb. per sq.in.	kg.persq.mm.	lb. per sq.in.	kg.persq.mm.		
1.	66,750 lb.	95.5 kg.	42,500 lb.	60.7 kg.	51.7	35.0
2.	76,000 "	108 "	45,000 "	64.2 "	45.8	30.0
3.	62,400 "	89 "	36,500 "	52 "	50.0	32.0
4.	69,000 "	98.5 "	37,800 "	54 "	44.0	28.0

Analysis					
No.	Si.	S.	P.	Mn.	C.
1.	0.23	0.025	0.044	0.74	0.19
2.	0.20	0.021	0.040	0.64	0.23
3.	0.27	0.043	0.036	0.52	0.19
4.	0.33	0.050	0.056	0.70	0.24

Of these samples Nos. 1 and 2 are from our basic furnace and Nos. 3 and 4 from our acid furnace. While the basic steel averages slightly higher than the acid steel, they are both very much better than the average results we were able to obtain from converter steel. The great superiority of the electric steel lies in the fact that these results can be consistently obtained from every heat, which we were never able to do in our converter practice. We have made physical tests on 30 consecutive heats and have for every heat obtained results corresponding to the sample above given. With converter steel we had great difficulty in maintaining an average reduction of area of 25 percent, and the elongation was usually about 20 percent.

The superiority of the electric steel was also manifested in the case of long, thin-section castings, such as cross-members on engine supports. Our loss due to shrink tears was much reduced when we were using electric steel. On one particular pattern we made 100 castings from electric steel, and found no shrink tears whatever. With exactly the same practice we found 90 out of 100 castings made from converter steel had slight tears or cracks, which had to be welded in order to save the castings. We might add that this particular casting was very difficult to make and was perhaps an extreme case, but the test we made brought out this difference in behavior most vividly.

The reason for this behavior is due no doubt to two facts:

1. The low sulphur contents of electric steel.

2. The absence of impurities, particularly of oxides. The absence of oxides undoubtedly gave the electric steel a much greater strength at higher temperature, and this greater strength was able to resist the pull, exerted on the steel during that period, when the castings were shrinking or shortening. This behavior of electric steel was true with both acid and basic steel, particularly with the latter, where we could maintain a lower sulphur.

Thus far we have emphasized the high quality of the electric steel, which was the one essential point which induced us to abandon the converter process in favor of the electric furnace. Our hopes in this regard have been most fully realized. We feel further that the time is now at hand when this fact will be fully realized by the trade at large, as is evidenced by the increasing demand for electric steel.

It was especially pleasing to have the higher quality steel without any increase in cost. Under present market conditions, with low phosphorus pig iron selling at an exorbitant price, the electric steel can be produced at much lower cost than converter steel. As our practice improves we feel confident that we can compete with converter steel even under normal market conditions.

At the present time we are using acid linings and bottoms entirely. Our reason for abandoning the basic process was the high and practically prohibitive price of magnesite. We were new consumers for this refractory and had not been able to secure a large supply, since the dealers were loath to take on new customers and we were finally obliged to resort to acid practice.

Our experience has been most valuable to us since we found one very great advantage in the acid process. One great difficulty with the basic process is the slag. Our metal was poured from the furnace into a large coffee-spout ladle, in which the metal was taken to the pouring floors. The metal was poured through a spout into hand shanks, from which it was poured into molds. In all cases the metal was skimmed by means of a metal rod skimmer, when it was being poured into molds, in order to keep all slag back and prevent its entering the molds. In spite of all precautions we had much more trouble from slag in our castings than we had ever had from converter steel.

With exactly the same methods this slag trouble disappeared when we changed to acid steel. This was due to the greater refractoriness or higher melting point of the siliceous slag, which brought about a more complete separation of the slag from the metal.

The basic metal acted at times as though there were actually present in the metal a small amount of slag in solution, which slag would finally separate, as the metal lost its heat. In a number of tests which were made, when special precautions were taken to remove slag from metal, during pouring of molds, we still found slag spots on the machined surfaces of our castings.

As already stated, with acid steel we have a minimum of slag trouble. This has led us to the conclusion that an ideal arrangement for a steel foundry would be to use a "reversed duplexing process," as it were. Part of your metal should be melted in a basic furnace, where the metal would be refined and sulphur and phosphorus be eliminated in the usual way. The stock used in this furnace could be of a much cheaper grade and would more than offset the increased cost of rehandling the refined metal through the acid furnace, as the next step in the operation.

In the meantime the acid furnace has been working on a partial charge of steel, to which, when molten, will be added the refined metal from the basic furnace. The final deoxidization under an acid slag can then be completed and metal withdrawn in same manner as we do now. The writer believes fully that this "reversed duplexing" can be so timed and manipulated in two or more furnaces that the ultimate output of the battery of furnaces will be the same in any given period as though the furnaces were all running either basic or acid independently.

This method of "reversed duplexing" would have several distinct advantages for the producer of steel castings, namely:

1. The cost of part of your raw material would be much lower, since you could use a high sulphur and high phosphorus stock, as for instance screw machine turnings, which bring a low price on the market and cannot be used in acid practice.

2. The basic furnace could be run at a lower temperature during refining period and the life of roof and walls would be much prolonged. The final temperature could be attained in the acid furnace, where we have no difficulty in securing necessary

temperature and fluidity without injury to lining, and we run up to 300 heats without repairing roof or lining.

3. We would be able to obtain lower sulphur and phosphorus in our acid steel without increase in cost; in fact the finished cost might even be less.

4. Our metal would receive final deoxidization under an acid slag. The advantage of this acid slag has already been emphasized, particularly the fact that slag is more refractory and separates more completely. There is one further advantage. When the furnace contents are poured into the large ladle the latter is immediately covered with a congealed heavy slag crust, which keeps the air away from the steel and also keeps the steel hot longer. This is of great help where pouring a large variety of small castings, where fluidity and high temperature are most essential.

The writer believes this reversed duplexing process may be of great value in other products such as tool steel, piano wire, etc., where the absence of even minute slag particles is most desirable. It would be interesting to conduct a comparative test on the products named above, made in the ordinary way and made by this double process. The suggestion may not seem so far fetched, when you bear in mind the fact that the higher grades of steel were, until very recently, made by crucible process, and in this process the slag was essentially an acid slag. How much of the quality possessed by these steels was due to the acid slag?

One other advantage of the electric furnaces should be mentioned, namely its great usefulness in making any of the alloys. This has been demonstrated by the constantly increasing adoption of the electric furnace by tool steel producers and other makers of special steel. This same advantage can also be put to use by manufacturers of steel castings in the production of alloy steel castings.

Our experiences in making alloys in the converter process was most unsatisfactory, since we were unable to obtain consistent results. This was due, no doubt, to the highly oxidized slag and presence of oxides in the steel itself, so that in many cases our alloys in metals were oxidized, and would be present in our final metal, in varying and diminished quantities.

With the electric steel our results have been very gratifying.

We have been able to obtain any desired analysis regularly, and in consequence our subsequent heat treatments have given us the high physical qualities which we were after. This opens up a large new field for the maker of small castings, since there is a large demand for alloy castings for certain purposes, when lightness and great strength and toughness are necessary.

In closing, the writer wishes to call attention to one fallacy so often mentioned in discussion of electric steel, namely this, that "electric steel is free from blow holes."

Many of you have read the article on "Hydroelectric Power and Electrochemistry and Electro-metallurgy in France" by C. O. Mailloux, the second installment of which appeared in the March 15, 1917, issue of *Metallurgical and Chemical Engineering.* Towards the end of the part treating on Electrosiderurgy there is a quotation from an article by M. Girod, appearing in 1912.

"With the electric furnace one is sure to have for castings an absolutely dense metal without blow holes or pipes."

Or to go even farther back, in an article appearing in 1907, in *Stahl und Eisen,* written by Professor Eichhoff, of Charlottenburg, entitled "Uber die Fortschritte in der Electrostahl-Darstellung," he writes, under his conclusions:

"Dass der Stahl vollständing blasenfrei ist."

Every producer of steel castings wishes that this might be true. Without doubt the electric steel is purer and in consequence has within itself a minimum of impurities, which during the transition from the molten state to a solid mass would assume a gaseous form and cause blow holes. This much is granted as true. But, nevertheless, there is just as much cause for presence of blow holes in electric steel where the metal is poured into molds, as when the metal is made by other methods. The cause for such blow holes is not inherent in the steel itself, but is due to the methods of making the mold and preparing same for the steel.

In other words, just as much care must be used in molding to make a good casting, in order to maintain in the casting the high quality and strength possessed by the electric steel. Perhaps even greater care and vigilance must be used because of the very high temperature at which the steel is delivered from the electric furnace.

We have merely brought up this point in order to emphasize

the fact that the electric furnace is not a cure-all for all foundry woes and troubles. To make a superior casting, the electric furnace metal must have a perfect mold, prepared with every possible care and attention to detail, properly gated, properly fed and properly vented. When such a happy combination has been properly brought about, the resultant casting will be superior, and in this manner only, and by no other methods can we derive the full benefit of the wonderful quality possessed by electric steel.

DISCUSSION.

R. F. FLINTERMAN: I have taken the opportunity to bring a small cast pinion. This is made of manganese steel, and is to be used on a pleasure automobile. It is rather a new departure in the steel casting industry. We can not possibly make these castings, unless we have intensely fluid steel, and it must be absolutely free from slag, for the reason that this casting must be ground and there is only one-sixteenth of an inch (1.5 mm.) metal removed from any surface, and any imperfection would show up immediately. This was ground down to a variation of one-half thousandth of an inch (0.0125 mm.) on any dimension.

G. P. FULLER[1]: I would ask Mr. Flinterman what are the yield point and ultimate strength of the casting described, having 36 percent elongation?

R. F. FLINTERMAN: With 0.25 percent carbon, running 60,000 to 65,000 lb. (42 to 45.5 kg. per sq. mm.) ultimate, the yield point will average pretty close to 60 percent of the ultimate; I think it will run about 40,000 to 42,000 lb. (28 to 29 kg. per sq. mm.).

ROBERT TURNBULL[2]: In regard to the acid bottom, do you consider that the acid bottom can be used with as much facility as the basic, or is there more trouble in using the acid bottom than the basic? Also, as there is no refining to be done in the acid process, would not the fixed type of furnace be as useful as the tilting type, particularly in view of the extra capital cost and troubles with the tilting type?

[1] Research Chemist, National Electrolytic Co., Niagara Falls.
[2] Maker of Electrode Regulators, Volta Mfg. Co., Welland, Canada.

R. F. FLINTERMAN: I can answer the first question by saying that the manipulation of the furnace is very much easier. We had a great deal of trouble at first because we could get no expert help on making steel for just our particular purpose, but we de-oxidized the steel very thoroughly, so that we could pour all of it without any addition outside of the furnace, completely de-oxidizing it. There is only one great difficulty, and that is refining, because de-oxidizing must be brought along and finished up at the time when you have reached the pouring temperature; because if it is delayed beyond that point, the slag gets so terribly thick, coming from the bottom of the bath, that we have a great deal of difficulty in doing anything with it, and very often have to pull that slag off. However, if the process is properly carried out, we very seldom have that difficulty.

As regards the fixed type of furnace, I cannot answer the question. I do not know how you would do it. Do you mean by tapping?

ROBERT TURNBULL: Yes.

R. F. FLINTERMAN: I would dislike to try it. We cannot get the slag out of a door eighteen inches square. It gets so terribly thick, and if they are negligent with it, it would gum up any holes that you could provide for its removal. After all, there is not much difference, except the first cost of your tilting furnace, and it is very much easier to maintain the spout in that way than by breaking through the furnace.

B. I. WHITING[3]: I think the author mentioned that with the acid bottom he took 350 heats out with one roof. I would ask how many heats the roof lasted on the basic product, and what the reasons for that difference in that case are.

R. F. FLINTERMAN: The reason is that there is a silica roof on a basic furnace, and with the degrees of temperature necessary to maintain, in order to pour castings successfully, the roof is constantly dripping down over the basic side-lining, and we never got over sixty to seventy heats on a single roof and lining. But that would be no criterion by which to judge of the process, because we were new and inexperienced, and I think that has been very much improved. Some of the operators are getting 150 heats

[3] Electric Furnace Engineer, C. W. Leavitt Co., Agents for Girod Furnace, New York City.

on a roof and lining. They are more careful in the selection of their fluxes, perhaps they changed their methods to some extent, so that it is very much easier on the roof and lining.

J. L. DIXON[4]: As to Mr. Flinterman's remarks on slag, we found that we secured greatly improved results in this way. Instead of having a pouring spout, we make a tap hole, tilt forward and pour the metal out through a hole four inches square, and we get most of the metal out before the slag comes. Many of the difficulties of slag inclusions in the steel are due to the basic slag striking the ladle before the steel does, and I think the more basic it is, the more it will bite onto the ladle, and perhaps gradually free itself as you are pouring out the metal.

Regarding the action on the lining, more especially the roof, when run on the acid process, obviously, there is an absence of fluxing action on the roof, but also the increased life of the roof may be due to the electric conducting properties of the acid slag. The acid slag has a very negative resistance coefficient, so that the current tends to go through the slag in one concentrated spot underneath the electrode and the arc does not wander around where it can radiate heat onto the roof. Also the acid slag is a much poorer thermal conductor than the basic slag, and, therefore, with the exception of those spots immediately under the electrodes, the upper surface of the slag should be comparatively cool and not capable of radiating much heat to the roof.

PRESIDENT F. A. J. FITZGERALD[5]: I think the question of the lime evaporation has a good deal to do with it. Some years ago Hansen described experiments made by him in the research laboratory at the General Electric Company, in which they made analyses of some of the stalactites that formed on the roof of a furnace, and found that these contained a high percentage of lime, which caused a great deal of the wear of the roof. (Transactions, **19**, 341.)

J. W. RICHARDS[6]: Perhaps some of the trouble met by Mr. Flinterman with the thick basic slag may be obviated by adding a small amount of acid flux, so as to more quickly reach the melting point. It is probably too basic, and the addition of some silica,

[4] Chief Engineer, J. A. Crowley Co., Detroit.
[5] FitzGerald Laboratories, Niagara Falls.
[6] Professor of Metallurgy, Lehigh University.

sand and feldspar in the right amount at the right time, may make the slag more liquid and improve his practice.

Regarding Mr. Flinterman's suggestion to use the reverse duplex, at the present time, good basic lining material being so very scarce, it might be well to consider that side of the question. The electric furnace requires a higher quality of basic refractory material than the open hearth, and in the present state of scarcity of magnesite of high quality, it might be more profitable to use a basic open-hearth furnace for melting, and refining the melt, and then transfer to the acid electric furnace for finishing. You could use then a poorer quality of basic material in the open-hearth furnace than would be necessary to give good results in the electric furnace. This is, of course, a temporary condition, owing to the scarcity of the higher class of basic material.

Regarding the general question of the fitness of electric furnace steel for steel castings, for the information of the Naval Consulting Board I sent a questionnaire to about forty or fifty of my friends in the steel business, asking how a better class of steel castings could be obtained. About nineteen out of twenty of these answers were that if they would specify electric furnace steel for their castings that, other things being equal, there was a far better chance of getting a fine casting from electric furnace steel than from any other class of steel.

Robert Turnbull: I do not quite agree with Prof. Richards as to the duplex process of the basic open hearth at the present time, and the latter being better than what Mr. Flinterman proposed. I think basic open-hearth material at the present time has decided disadvantages over what can be used in the electric furnace. The electric furnace can utilize all steel turnings, which is the cheapest raw material you can buy at the present time, and as there is a tremendous tonnage of that class of material being purchased, I think the combination of the basic electric and the acid electric would be cheaper, and the latter could be erected and put in place quicker than the open-hearth.

One electric furnace, of say 6-ton capacity, with enough power behind it, could melt and refine as quick as the acid furnace, so practically two electric furnaces would do the work, instead of having a very large open-hearth, which would be necessary. I would be inclined to favor the two electric furnaces in the duplex process.

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 3, 1917, President FitzGerald in the Chair.

THE BETHLEHEM 10-TON GIROD STEEL FURNACE

By C. A. Buck.

[*Abstract.*]

A description of the 10-ton Girod furnace now in operation at the Bethlehem Steel Company's plant in South Bethlehem, Pa. Details are given of the building, the platforms, arrangement of bins, the dimensions and equipment of the furnace proper, particularly the devices for raising and lowering electrodes and for preventing induced currents in the shell of the furnaces. Details are given of the general operation using cold charge, the refining by slags, composition of the slags and of a variety of steels made in the furnace.

The 10-ton Girod electric steel furnace made its first heat May 16, 1916, and has made a fairly consistent run to date. Until September 1st the furnace operated on single turn, but since then has been in continuous operation, except when down for repairs or power. To date (February 23d) 247 heats have been made, and the quality of steel produced has been gradually improved.

The electric furnace building is 168 ft. (50 m.) long and 58 ft. (17 m.) wide, served by a 30-ton crane. The charging platform, which is elevated 12 ft. 3 in. (3.6 m.) above floor and yard level, extends 14 ft. 6 in. (4.2 m.) beyond building columns along the outside of building wall. On this extension there are covered bins for refractory materials, flux, ore, alloys and scale, these materials being unloaded from cars and stored.

The furnace proper, which is located above the charging platform, is cylindrical in form and made of ¾-inch (1.9 cm.) steel plate, approximately 15 ft. (4.5 m.) in diameter and 5 ft. (1.5 m.) outside depth, with laminated outside plates, ¾-inch (1.9 cm.) thick. It is equipped with one heavily-laden, counter-balanced

charging door, sliding in a water-cooled frame. The pouring spout is directly opposite. On the side of the shell heavy copper angles are attached to which are electrically connected laminated copper bars conveying current from the transformers.

The furnace rests on heavy cast-iron rockers running on rollers supported by rocker frames anchored to concrete foundation. The tilting of the furnace is accomplished by means of worm drive, actuated by a 15 h. p. motor. The furnace can be tilted toward the charging side to discharge the slag through a notch in the charging door, or toward the pouring side to pour the molten metal into a 12½-ton ladle located in the pit in front of the furnace. The bottom, 20 in. (50 cm.) in thickness, is made of double burned dolomite well rammed in with tar. The metal bath is approximately 16 in. (40 cm.) thick.

Fourteen soft-steel poles approximately 3½ in. (9 cm.) in diameter are connected electrically to the bottom of the furnace shell, the lower ends being water cooled. The roof construction, which is arched, consists of 9-inch (23 cm.) silica brick, insulated from the magnesite brick of the hearth walls by means of asbestos plates, with provision for reception of three 17-in. (43 cm.) amorphous carbon electrodes. The electrode coolers in the roof are made of copper and are water cooled.

Ample provision has been made for adjustment, so that electrodes can be adjusted and centered firmly and speedily. Two laminated copper bars carry the current from the transformer to the contact pieces extending from the electrode carrier. The lowest point of an electrode during operation of the furnace is approximately 4 in. (10 cm.) above the surface of the metal bath.

The electrodes are raised and lowered by means of a revolving screw spindle centered in the structural column, which is driven by a 5 h. p. motor, mounted at the foot of the column, or, if necessary, it can be operated by means of a hand wheel. The total weight of one electrode-carrying column is approximately 2,600 lbs. (1,180 kg.) the weight of an electrode being about 1,000 lbs. (450 kg.).

The motors employed for this work are reversible, interpole type, using direct current at 230 volts, equipped with automatic speed regulation. The total weight of the furnace is approximately 90 gross tons, which includes about 35 tons of refractories.

About 1,500 KVA of 3-phase alternating current, 25 cycles, 65 to 80 volts, is furnished to the electric furnace, each electrode receiving one phase of a 3-phase current, the conducting hearth of the sheel acting as the neutral point. Special care has been taken to prevent the formation of induced currents in the shell and the roof frame, and to prevent sparking from the bus bars at the lower end of the electrode-carrying column to that column in electrical contact with the shell.

The current is conveyed to the furnace from three water-cooled single-phase transformers of 700 KVA each. It is generated by Bethlehem gas engines driving 2,500 kw. generators, producing 3-phase alternating current of 6,600 volts at 25 cycles. One reactance coil of 106 KVA capacity has been provided for the protection of each transformer. A special controller for each electrode is mounted in front of the switchboard, and one controller is provided near the pouring spout for the operation of the tilting motor. The transformers are sheltered in rooms underneath the charging floor on both sides of the furnace, while the reactance coils and oil switches are in another room. The high-tension conductors are well insulated cables, the low-tension conductors are heavy bus bars laminated only where flexibility is required.

Of the 700 KVA leaving the three transformers, about 620 KVA actually reach the electrode holder, the balance being lost in the form of heat through water-cooling, etc. The consumption of cooling water at the furnace is about 20 gallons (75 liters) per minute.

The yield from cold charge to finished ingots is about 92 percent.

A thoroughly equipped laboratory erected for the open-hearth department, which is adjacent to the electric furnace department, takes care of the necessary testing of the steel, etc. The electric furnace will become a valuable adjunct to the Bessemer converter and the open-hearth furnaces, as a means of refining their molten product.

It is believed that the greatest field for this grade of steel will be in the alloy steel market and for many grades of tool steels. Thus far the following steels have been made: 1.5, 2.5, 3.5 percent nickel, nickel chrome with 0.50 chromium, chromium

vanadium, and simple carbon steels ranging from 0.08 to 1.30 percent carbon.

The materials used for steel making are as follows: scrap rails, high-phosphorus turnings, billet crop-ends, drop-forge trimmings, etc., which mixture should average 0.040 sulphur.

The operation of the furnace is very similar to that of the basic open hearth. Following the tapping of a heat, turnings are charged and leveled down. Any necessary repairs along the slag line are made with dolomite. Billets or other heavy scrap are next charged, followed by turnings until the entire 21,000 lb. (9,550 kg.) charge is in the furnace. Lime is then added, current turned on, and melting is begun. Much of the phosphorus is removed through combustion, carbon is reduced by oxidation, and some of the sulphur is removed. The length of time required for the oxidation is dependent upon the carbon and phosphorus content of the charge.

When it is considered that the oxidation has proceeded far enough, a test about 2.5 in. (6 cm.) diam. and 2 in. (5 cm.) long is taken, forged under a hammer, quenched in water and bent through 180 degrees. When the test bends without breaking through the bend, the oxidizing slag is removed by tilting the furnace backward and skimming off slag through the charging door. Slag flows through a chute in the charging floor into a slag car under the floor.

Following removal of the oxidizing slag, the recarburizer is added, followed by the deoxidizing slag of powdered petroleum coke, silica sand, lime and fluorspar. This slag dissolves ferrous oxide which has formed on the surface of the bath.

A reasonable time after the addition of the deoxidizing slag a test is taken for the laboratory for carbon determination. Varying amounts of ferro-silicon, ferro-manganese, etc., are added to bring the slag to the point where it becomes white, and quickly disintegrates into a fine white powder. These alloys act very energetically on the oxide in the bath, forming a very fluid slag, which easily rises to the surface. During this period, when the slag is completely deoxidized and is very basic, the desulphurization, which was incomplete during the first stage of the operation, proceeds further, and is rapidly completed at the time of tapping.

The average analysis of the preliminary tests taken after the charge is melted and before removal of oxidizing slag is as follows:

C. 0.07 Mn. 0.11 P. 0.008 S. 0.036 Si. 0.022

The analysis of oxidizing slag from heat Y-1219, a high-carbon simple steel heat, and of the finishing slag at time of tapping showed—

	Oxidizing Slag	Finishing Slag
SiO_2	8.89	6.49
FeO	36.82	1.26
MnO	4.71	0.16
CaO	35.26	69.83
MgO	9.25	2.61
P_2O_5	0.705	0.092
S	0.19	0.34

This heat finished with phosphorus 0.010 and sulphur 0.016. Several heats have been made since this one analyzing below 0.010 P. and 0.015 S.

All of these heats are entirely satisfactory from a metallurgical standpoint. The ingots rolled well, and in many cases it was not necessary to chip a single billet.

Nearly all of the heats thus far have been cast in 19 x 19 in. (48 x 48 cm.) x 6,000 lb. (2,730 kg.) or 21 x 27 in. (53 x 68 cm.) x 12,000 lb. (5,550 kg.) ingots, and the practice on the 35 in. (88 cm.) bloomer mill on the various grades has been from 75 to 82 percent.

DISCUSSION.

E. B. Pratt[1]: Mr. Buck says that special care has been taken to prevent the formation of induced currents in the shell and the roof frame, and to prevent sparking from the bus-bars at the lower end of the electrode-carrying column to that column in electrical contact with the shell. Will Mr. Buck kindly explain in detail how this is accomplished, what materials are used as insulators, and how and where these insulators are inserted?

Bruce I. Whiting[2]: The direct magnetic loop of the control is broken up by non-magnetic territory, either copper, brass or

[1] Mutual Benefit Life Insurance Co., Cleveland.
[2] Engineer, C. W. Leavitt Co., Agents for Girod Furnace, New York City.

silica steel, or manganese steel, although manganese steel is hard to work. Any material that is non-magnetic can be used for that purpose. The insulation of the column over the shell to prevent short circuit is made by inserting mica, and it is also placed in the roof and the shell, to prevent any possible short circuit in case the roof becomes sufficiently hot to become conducting.

The furnace at the Bethlehem Steel Company's plant is circular. The impression seems to have gained ground that the Girod furnace is square. It was in the past, but as many furnaces have been changed in design, so has the Girod furnace. It is now being built circular, being more efficient thermally, and permitting the use of three electrodes, instead of four, as was formerly the case. In the old furnace four square electrodes were used, and now there are three with the bottom contact. The use of the bottom contact in the design of the furnace permits the use of dolomite for the bottom material, instead of the more expensive magnesite, and permits the use of the cheaper refractory, especially at this time, which is very important.

The small sizes of the Girod furnace are not made in the same way as the 10-ton furnace mentioned here. As you get to the smaller sizes the use of the three electrodes produces greater mechanical difficulties and entails greater thermal losses.

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 3, 1917, President FitzGerald in the Chair.

RENNERFELT ELECTRIC FURNACE OPERATION

By C. H. vom Baur.

[*Abstract.*]

The paper deals with improvements and changes in the Rennerfelt furnace intended to better adapt the Swedish design to American practice, and particularly in the following respects: (1) The furnace here is now made circular with one set of electrodes, and oval shape with two sets; (2) the side electrodes are adjustable in a vertical plane, allowing them to dip toward the bath; (3) the power for a given size furnace has been largely increased.

The results of these changes have been longer life of refractories, reduction in power per ton of metal melted and treated, and greater tonnage per day.

Some decided improvements have been made in the design, and consequently the operation, of the American Rennerfelt electric furnaces, since my description of this apparatus before the Society at the twenty-ninth meeting (April, 1916). Briefly these consist of the following:

1st. The furnace hearth is now circular, with one set of electrodes, and oval shaped with two sets.

2d. The side electrodes are adjustable in a vertical plane, allowing them to dip towards the bath.

3d. The available power, or instantaneous available heat, has been largely increased.

The operating results obtained in making these three changes have not only kept up the quality of the steel, but the cost has been reduced materially. The reasons for this are quite apparent.

With a circular hearth and the flame in the center, the heat distribution is equal at the slag line, there are consequently no

cold corners, obviating overheating when melting, which is so detrimental to both side-walls and roof. The side-walls, slag-line and roof, especially the latter, now dome-shaped, are easier to repair. Often, only the center portion of the roof bricks need replacing, the other roof bricks lasting twice as long.

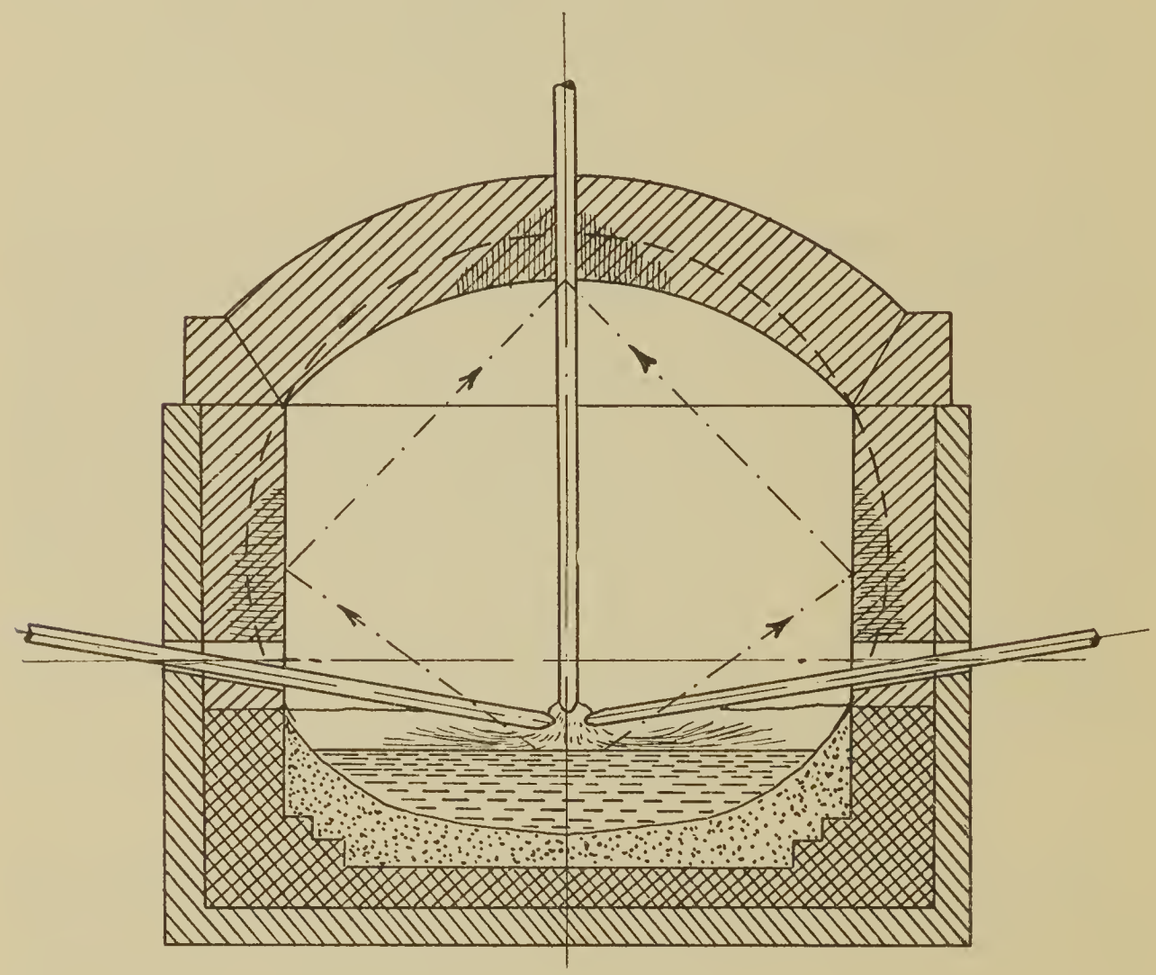


Fig. 1.

In the accompanying sketch, Fig. 1, the shaded portions show how the refractories, either basic or acid, wear out first. The portions of the central part of the roof being directly over the flame would naturally wear more there, and it seems that this is accentuated by reflection from a too thick slag first reflecting from the side-walls substantially as indicated by the broken lines. The dotted lines show the tendency toward eventual wear.

The second feature, viz., tipping the side electrodes down from a horizontal position, has several advantages. When smaller charges than normal are made, the most efficient height over the metal when melted can be had. During melting, the electrodes

at the start, whether for partial or full heats, are usually only an inch or so (2.5 cm.) over the bath. As the charge melts, the electrodes are continually lowered, thus keeping the flame about 2½ to 3 inches (6.2 to 7.5 cm.) over the bath. Bringing the flame closer to the bath accomplishes two things: the melted steel more readily absorbs the heat, and the large flame being farther away from the roof, lengthens its life. This is proven by the shorter time to make a heat from a cold charge and by a longer life of the roof.

The possibility of tilting the electrodes up and down helps when slagging off, and lessens the breakage of electrodes.

The flame nearer the bath, and with the same potential has a tendency to circulate the slag faster. This can easily be observed, and is of the greatest importance. A more shallow bath facilitates the refining, as the metal comes in contact with this slag on a larger surface.

The flame itself, depending on the size and electric power of the furnace, seems to make a circular patch on the thinned slag directly beneath the flame about 8 or 10 inches (20 to 25 cm.) in diameter, and then mushrooms out. The hotter the furnace, the better the conductivity of the gases and the greater the spreading of the flame. In a two-flame furnace, this flame at times seems to spread over the entire bath. This appearance is, no doubt, due to incandescent gas. The hearth is made more shallow, and thus the rammed-in bottom coming up at the sides makes the sides less steep. This shallow bath shortens the time of melting down, and the lining is less affected at the slag line.

The regulation of the heat applied to the bath is made easier by the variable position of the flame above it, and it also lessens the danger of overheating, which is apt to become so detrimental with an acid bottom. The almost invariably clean steel produced, with the absence of inclusions, is obtained by careful handling, yet the ease of avoiding overheating is of first importance. Metallurgists who have operated the Rennerfelt furnace have particularly noted this length point, and the avoidance of worry which thus ensues.

Having the electrode tips never more than 3 inches (7.5 cm.) above the bath, has materially reduced the time of melting (so far no Rennerfelt furnace in the United States is using fluid

charges). With basic bottom the dephosphorizing time has remained unchanged and the desulphurizing period, with the aid of calcium carbide slags, has been reduced. When refining and reducing sulphur with a built-up slag from ferro-silicon and lime, as used in the induction furnace, this was accomplished with good effect.

With furnaces having 300 K.W. power per ton of output, heats have been made on basic bottoms, taking off one slag in 2½ hours with 670 K.W.H. per ton when operating continuously. With acid bottoms and 200 K.W. power per ton of output, taking off one slag, good steel and full heats have come off in 3¼ hours, with 635 K.W.H. per ton.

The electrode consumption is less than six pounds (3 kg.) per ton of steel made, operating continuously. Even with the present excessively high cost of refractories, this cost has been reduced in the smaller furnace of one ton from $2.91 per ton of steel made to less than $0.80 per ton. Roofs are lasting over 100 heats, and approximate the longer life made in Europe with better refractories. With a higher power input the heats are shortened, due to the smaller melting period (the heat being considerably reduced during the refining time) thus roofs are lasting more heats than formerly, though the actual time is not much changed. Side-walls of brick outlast two or more roofs, while the bottom lasts a year or two.

The third change, to higher powered furnaces, besides lowering the cost per ton in every way, steadies the consumption of electricity, which has already been very constant. For instance, a 3-ton furnace operating with 600 K.W., with hand-regulated electrodes, will reduce in four or five minutes to about 550 K.W. without any fluctuation (except during the first part of the melting period) and without touching the electrode regulating mechanism. With smaller furnaces the steadiness is not so marked, whereas with still larger ones, the effect is but little improved. The power factor is about 90 percent, with 60 cycles. All sudden strains on the power supply are avoided. The arc voltage has been raised, and is now 110 to 120.

In general, too much stress cannot be laid on the various small details, such as tight doors, and tight openings around the elec-

trode cooling boxes. With the latter, besides a small clearance between the cooling box and electrodes, asbestos washers help materially.

Regarding non-ferrous metals, the results published (in Vol. 29, year 1916) have frequently been duplicated and in some instances bettered. For instance, railway journal-bearing metal (70 percent copper, 10 percent tin, 15 percent lead, and 5 percent Zn, Mn, Fe, and impurities) was melted in a hot furnace in 29 minutes, and with less than 160 K.W.H. per net ton. Aluminum-nickel alloys were melted in less than 15 minutes, consuming about 300 K.W.H. per net ton.

DISCUSSION.

C. H. VOM BAUR: There is a point I have not mentioned in this paper which may be of interest in connection with the next to the last paragraph on page 89, in which it is stated: "The almost invariably clean steel produced, with the absence of inclusions, is obtained by careful handling, yet the ease of avoiding overheating is of first importance." When melting copper in a type of furnace where the bath conducts current, such as in the Heroult type, the copper melts very nicely, and the copper ingots are very satisfactory. But the volatilization loss is high and the fumes given off so great that the crew became poisoned and the tests were not again taken up. In using the Rennerfelt type of open arc, which is from three to four inches above the bath, this volatilization loss is very low. The average loss in six weeks' run, melting pure copper, was two-thirds of one percent. One week it was as low as three-tenths of one percent, and no appreciable fumes given off to cause any complaint. I should like to hear some discussion on that topic.

The electrical circuit on this furnace is very simple. There is only one high-tension switch, a three-pole, single-throw overload release, and the low-tension circuit has only a set of two choke coils, with four single-throw, single-pole knife switches.

Sometimes, in charging the furnace, the automatic electrical control is applied. The current consumption and electrode regulation is, however, quite satisfactory with hand regulation. As much as 600 or 700 kilowatts is used on one set of three electrodes.

H. W. GILLETT[1]: As I understand it, the figures given in this paper for the power consumption in melting a bearing bronze, were obtained by putting the charge of bronze into a furnace normally used for steel, after a heat of steel had been taken off, and noting the power used before the bronze was ready to pour. Inasmuch as this bronze is poured at about 1,100° C., and steel at, say, 1,600° C., there must have been a considerable amount of stored heat in the lining of the furnace that was aiding in the melting of the bronze and reducing the needed power input well below that needed had the furnace been only at bronze-melting temperature at the start, instead of at steel-melting temperature. Hence, while the experimental data are doubtless correct, the conclusion drawn as to the low power consumption on bronze, is probably not correct. Will the makers of this furnace guarantee the power figures given for non-ferrous alloys in this paper, or in the one presented at the last meeting?

Is the same arc voltage used on a Rennerfelt furnace for brass as on one for steel? Are there any difficulties in holding a steady arc when melting brasses very high in zinc?

C. H. VOM BAUR: This test mentioned at the end of the paper was made in a second heat on Monday morning, after the furnace had been standing idle since Saturday, and of course the furnace was not at a steel-melting heat. The furnace was no doubt hotter than what it would be ordinarily for the melting of brass.

Regarding Mr. Gillette's other question, perhaps when yellow brass turnings were melted, fifty percent were of the ordinary size, and the remainder was yellow brass in chunks. The loss was 6.4 percent, which is considered high. The voltage on a furnace of that kind usually runs at about eighty or ninety, whereas it usually runs about 110 or 120 with the steel furnace.

H. M. ST. JOHN[2]: I have had a little experience with a bearing bronze similar to the one to which Mr. vom Baur refers, and

[1] U. S. Bureau of Mines. Ithaca, N. Y.

[2] Research Engineer, Commonwealth Edison Co., Chicago, Ill.

I certainly find it difficult to make myself believe that an average figure for energy consumption on bearing bronze would be anywhere near as low as 160 kilowatt-hours per ton. That is something which will have to be proven; but it seems to me that a figure of that sort would have to be accepted with some question, until it could be backed up with a long series of tests.

As to the difference in the volatilization of copper with an indirect-arc furnace and direct-arc furnace, I have had a little experience with a direct-arc furnace, running on a high-copper alloy, in which there was considerable volatilization of copper and lead. Although the furnace has been running for a long period of time, there never have been any signs of poisoning effect such as that mentioned by Mr. vom Baur. There has been some sign of poisoning which I ascribe as more probably due to the lead or possibly the antimony, which was also given off from the furnace, an effect very similar in its characteristics to brass shakes, as the brass founders call it; in other words, similar to zinc poisoning, although there was no zinc present in the alloy.

M. H. BENNETT[4]: In regard to the test on copper, is that a gross weight test? By that I mean the pounds charged divided by the pounds poured. If not, what was that figure? What was allowed for the skimmings, and what was found? And if there was any copper in the skimmings, what percentage was it of skimmings? Also as to the linings, how much metal was in the linings, and what percentage of the total? In other words, these metal figures are often given so loosely as to be of very little value in the commercial field.

I have some figures from our crucible experience showing a gross loss of 7 percent, while the net loss was 1.8 percent, but that which we reclaim out of the skimmings and linings costs us so much to reclaim, we might as well have lost it.

Another thing the author speaks of is the making of good copper castings in this type of furnace. Was the copper a standard deoxidized, high-grade copper, or copper that had oxygen in it, how much free gas was there in the casting, and what num-

[4] Research Engineer, Scovill Manufacturing Co., Waterbury, Conn.

ber of castings were there? I have always maintained that in a furnace having an atmosphere high in CO, as in a furnace of this type, the oxides in the copper should be reduced. I have heard many people say that the reducing carbon must be in actual contact with the copper, but I believe the gas is equally effective, and I would like to know if the author has had any experience which would bear on this point.

In regard to the melting efficiency, 160 kw. hr. per net ton, I was checking that up against Dr. Richards' metallurgical calculations, and the figures are about 104 percent. I think there must be some mistake; some stored energy somewhere.

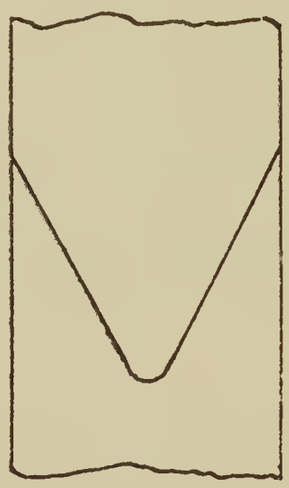


FIG. 2.

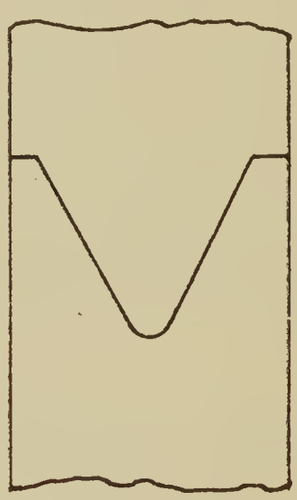


FIG. 3.

J. W. RICHARDS[5] (*Communicated*): Taking Ledebur's value of 130 calories per kilogram of melted bronze, the thermal efficiency would reach 89 percent, which is probably too high, but is not an impossibility.

C. H. VOM BAUR: This copper loss mentioned would allow for the usual spills and skulls. This copper was poured mostly into small castings, for dynamo brush holders on direct-current machines, made in the works of one of the largest dynamo manufacturers.

I cannot answer the questions of Mr. Bennett. I did not investigate. As this concern has ordered another furnace, I think that perhaps will be the best answer to that question, as far as blow holes in these castings are concerned.

[5] Professor of Metallurgy, Lehigh University.

E. B. PRATT[6] (*Communicated*): What has been the experience in regard to breakages of electrodes, especially the two side electrodes?

How are these two side electrodes operated and adjusted, both in respect to hand regulation as mentioned on page 90 and mechanical regulation as mentioned on the same page? I would like to see detail drawings of this mechanism to see how it compares with the similar regulating mechanism of the Stassano type of furnace in which the electrodes enter the furnace at about the same angle.

C. H. VOM BAUR: That is largely a question of taking care of the electrodes. I have seen many people break their electrodes, and I have seen electrodes that have run two days without being broken. It does not seem that the side electrodes break off any easier than the top electrodes, if care is taken.

As this question has come up, I would say that the cone type joint, with the cone starting at the surface is stronger than the joint having a shoulder between the surface of the electrode and the cap of the same. I think that is of importance to every one who uses furnace electrodes. (See Figs. 2 and 3.)

F. A. J. FITZGERALD[7]: Before that was used, did you have trouble with the electrodes breaking at the joint?

C. H. VOM BAUR: They would break, but not of their own weight. They usually broke when you hit them, or when, by improper adjusting, the top electrode would strike against the side electrode, and you would probably break off the top one. The cone type seems to be a stronger one; for instance, when the air leaking into the furnace is excessive, the joint of the first cone type (Fig. 2) will last longer than the second (Fig. 3).

M. H. BENNETT: May I ask about what amount of angle there is in that type?

A. N. WILLIAMSON[8]: The angle is about 50 degrees in that joint.

J. W. RICHARDS: I think we should pay more attention to the volatilization of metal in the furnace. I notice Mr. vom Baur

[6] Mutual Benefit Life Insurance Co., Cleveland.
[7] Electric Furnace Engineer, FitzGerald Laboratories, Niagara Falls, N. Y.
[8] Chemist, Acheson Graphite Co., Niagara Falls, N. Y.

speaks of the gases becoming more conducting the hotter the furnace. The greater conductivity is probably largely due to the metal vapors which rise only a little way above the surface of the metal and increase the conductivity of the gases in the neighborhood of the arc.

I have seen an arc six inches long, with only 100 volts on the furnace; much like a mercury lamp arc, but on a different scale. I have been making estimates of the vapor tensions of the metals at these furnace temperatures, and have obtained data with which, I think, we can commence to take them quantitatively into account.

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 3, 1917, President FitzGerald in the Chair.

ELECTRICAL CHARACTERISTICS OF ELECTRIC FURNACES.

By A. A. Meyer.*

[*Abstract.*]

An electrical investigation of a Heroult and of a Grönwall electric steel furnace, covering their construction, operation, load fluctuations, power factors, unbalancing effects on the three-phase system, and determining of the wave distortion by the oscillograph. The oscillograph data are studied closely, to draw from them deductions as to the self-induction of the furnace and connections. The effect of these considerations on the accuracy of the customer's watt-hour meters is also discussed.

In this paper the author wishes to present the results of a few investigations made on two types of electric furnaces. One is the Heroult, the other the Grönwall; both being supplied with energy from the Detroit Edison Company's system.

It is well known that the fluctuations of any electric furnace are rapid and at times violent, and due to the unbalancing of such load on the different phases of a line feeding from a substation bus, the fluctuations are apt to be annoying to the central-station system. In view of the severe fluctuations, tending to distort the wave shape of the energy supply, a question arose concerning the accuracy of the customer's watt-hour meter. In addition, there was the question of the power factor of such a load.

With these questions in mind a few tests were conducted on these two types of furnaces to analyze the various electrical factors involved, to determine the relation of these factors, and to ascertain, if possible, how significant or serious they are.

The two furnaces under consideration, *viz.*, the Heroult and the Grönwall, are both of the short-arc conducting type in which

* Assistant Electrical Engineer, The Detroit Edison Company.

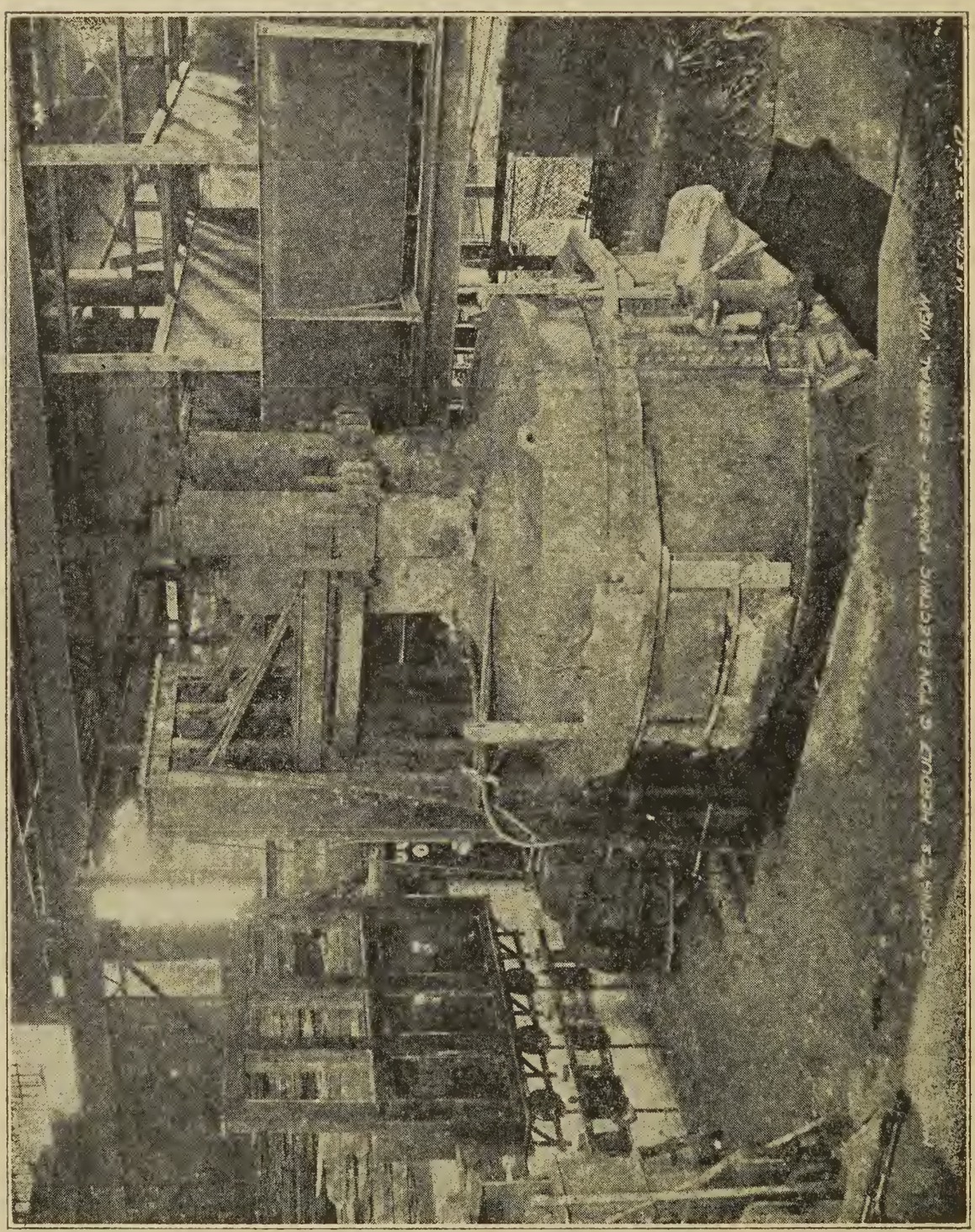


FIG. 1.

the arc strikes from the electrodes to the metal charge, the latter being used as part of the path for current to pass from one phase to the other. Both of these types being well known in this country, the author will not go into any lengthy description, nor discuss their relative merits. However, for the benefit of those readers not so conversant, and in order to make the discussion of this paper perhaps a little clearer, a brief description with some pictures and a few simplified wiring diagrams are included.

The Heroult Furnace.

The Heroult type furnace is being operated by the Michigan Steel Castings Company, of this city, for making steel for steel castings. There are two such furnaces installed in their plant, one a six-ton and the other a three-ton. Only the larger of the two will be referred to in this paper. Fig. 1 is a picture of it, showing an elevated floor built around it, from which the furnace is charged and operated. The main floor for pouring, etc., is directly below this. The furnace has an acid lining composed of silica formed into a shallow hearth, and a roof of silica brick. There are three openings in the sides, one forming the pouring spout and the two others the charging doors. The furnace is supported on curved rails set in a concrete foundation, and is provided with a motor-operated gear mechanism for tilting the furnace proper with its electrodes and bus connections. Fig. 3 is a sort of longitudinal section combined with a simplified diagram of electrical connections.

There are three 17-inch (43 cm.) amorphous carbon electrodes projecting vertically through the roof and through water-cooled collars, each electrode being held securely by a steel beam extending out from the rear of the furnace and over the roof. This beam is free to move up and down, according to the desired height of the electrode. Regulation of the electrodes or length of the arc is controlled in two ways: either manually by means of a hand controller operating a D. C. motor, or else automatically by means of a Thury regulator in connection with the electrode motor, the regulator being set to govern a predetermined constant value of current in the secondary bus lead to each electrode. One feature of this regulator is the movement of the electrode in a series of small steps, each step requiring a small definite interval

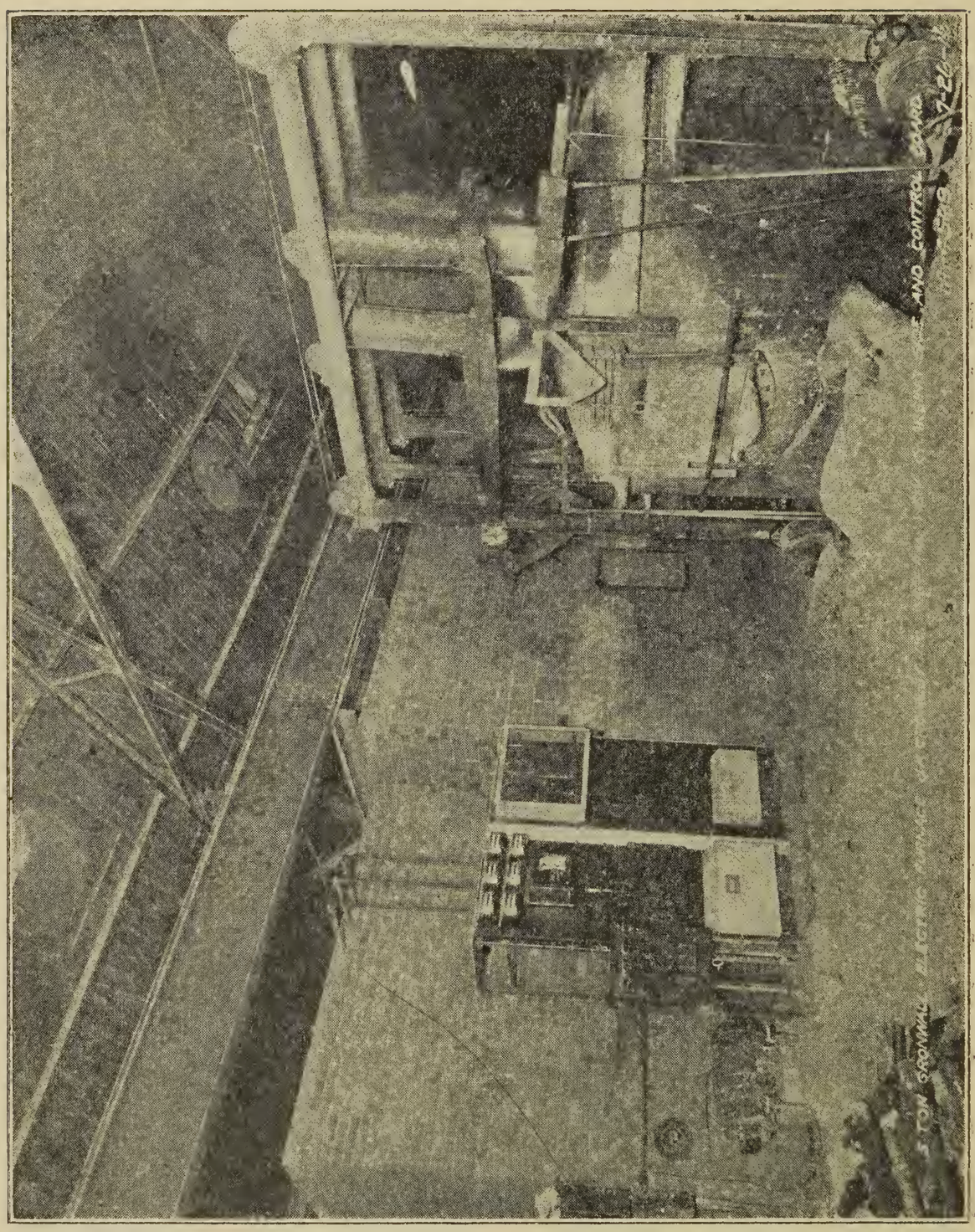


FIG. 2.

of time. Either the manual control or the automatic regulation is effective at any one time, and the control of any one electrode is independent of the other two.

The furnace is rated at six-ton capacity, taking 1,200 K.W., three-phase, 60-cycle energy at 110 volts. This service is obtained from a 4,600-volt bus in the customer's plant through a bank of three single-phase transformers, connected delta-delta and located close to the furnace, as shown in Fig. 3. The transformers are not loaded with any other load except that of the furnace. They are oil-insulated, self-cooled and rated at 400 K.W. each. Their inherent reactance is 5 percent. The connection from the bus to the transformer is made through an oil switch which is hand controlled, but with an automatic tripping device for heavy overload protection. The customer's bus is supplied from a central-station substation by means of a 200,000 c. m. (1 sq. cm.), 3 conductor, 4,600 volt cable about 12,000 ft. (3,600 m.) long and serving no other customers along its route.

The metering of energy supplied to the customer is done on the 4,600-volt bus by means of an induction type watt-hour meter connected to current and potential transformers. The meter is a Fort Wayne, type K-3, 3 ampere, 110 volt, 60 cycle meter, and the current transformers are General Electric Co., Form K-28, with a 300 to 5 ampere ratio. The potential transformers are General Electric Co., Form AQ, 200 watt, with a 4,400/110 V. ratio. The connections for metering are shown in the diagram of Fig. 5.

The bus connections from the transformer to the electrodes of the furnace are of interest in view of some of the tests that were made to study their electrical properties. Each phase is built up of part solid bus bars and part flexible cables, the latter to accommodate tilting of the furnace. Between points 1 and 7 in Fig. 3, the bus consists of eight pieces ¼ x 6 in. (0.6 x 15 cm.) copper bars in each phase about 7 ft. (2 m.) long, spaced triangular with 20 inches (50 cm.) between phase centers. The flexible leads, about 19 ft. 6 in. (5.8 m.) long, consist of nine 1,000,000 c. m. stranded bare copper cables in each phase, tied around the periphery of small spacers placed at frequent intervals. The bus connections from point 2 to 3 are made up of ¼ x 6 in. (0.6 x 15 cm.) copper bus, six bars in each phase and extending first

vertically between the beams of the steel structure in the rear of the furnace and then horizontally out to the electrodes; the total distance from point 2 to 3 being about 14 ft. 6 in. (4.35 m.). All three phases are spaced in the same plane with 20 inches (50 cm.) between phase centers.

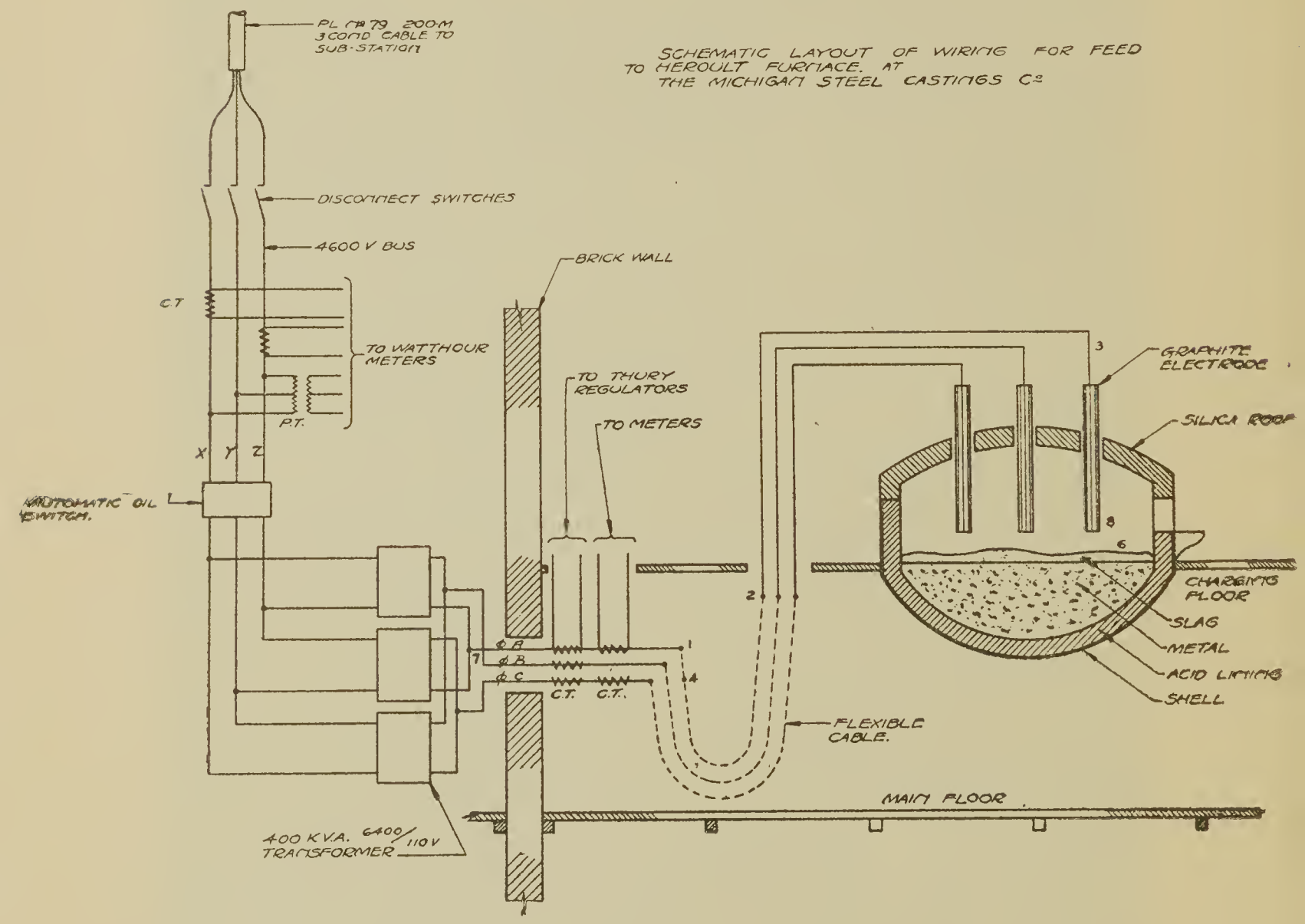


FIG. 3.

For guidance in operating the furnace, indicating watt-meters are installed in each phase. These watt-meters take their current from special Westinghouse current transformers connected in the secondaries of the power transformer. Separate from these current transformers there is another set of current transformers for operating the Thury regulators.

Grönwall Furnace.

The Grönwall type furnace is being operated by the J. A. Crowley Company of this city for the production of high-grade alloy

steel. There are two such furnaces, one a five-ton, operating at the present time, and a ten-ton now being installed. Fig. 2 is a picture of the five-ton furnace as it stands on the floor, and Fig. 4 is a simplified diagram of the electrical connections. The furnace has a lining of dolomite, forming a shallow and conducting

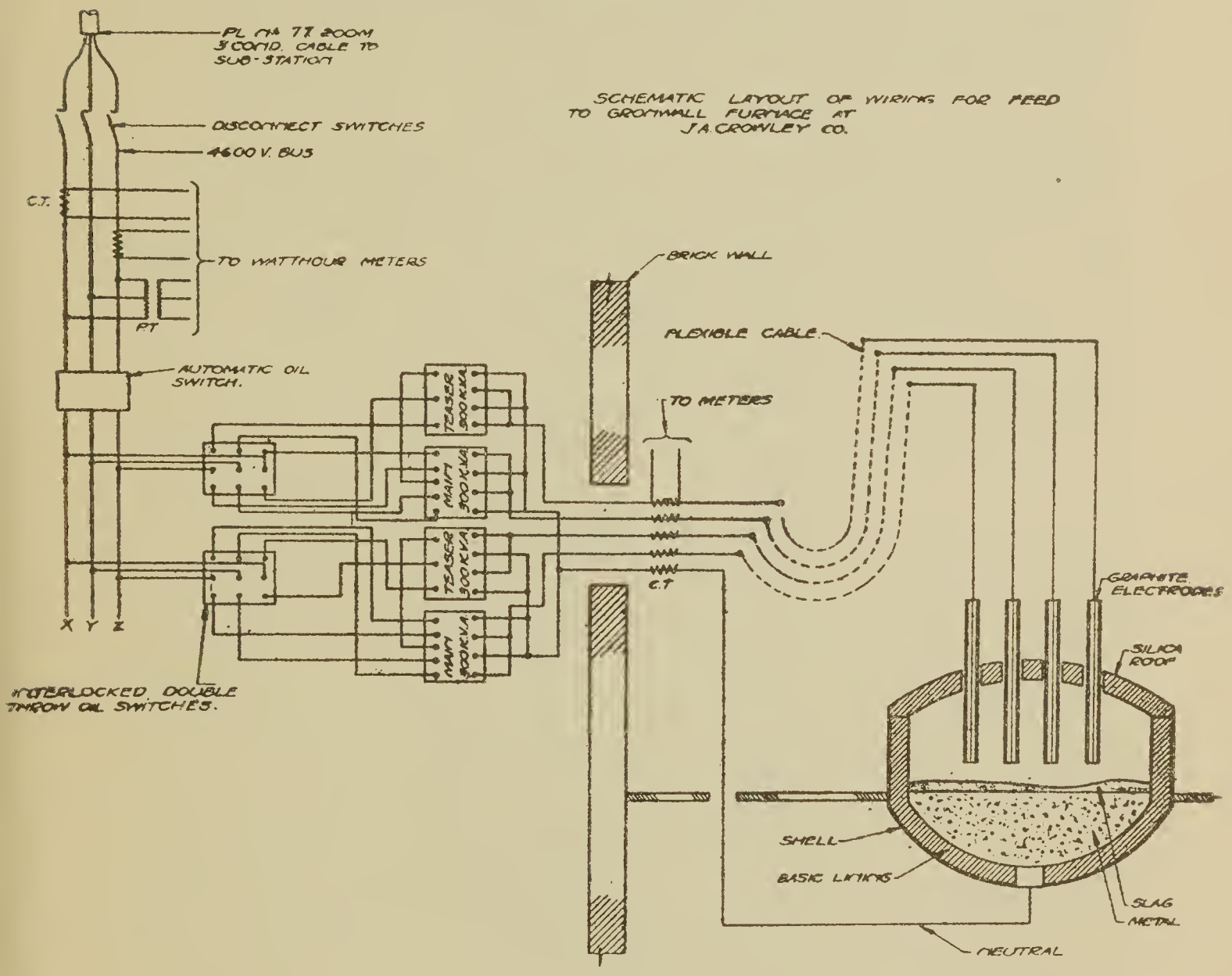


FIG. 4.

hearth, and is covered with a roof of silica brick. There are two openings in the sides, one the charging door, shown in Fig. 2, and the other the pouring spout, diametrically opposite the former. The furnace is supported on curved rails on a concrete foundation, and is provided with a motor-operated gear mechanism for tilting the furnace with its electrodes and bus connections.

There are five electrodes, four projecting vertically down through the roof and through water-cooled collars, and the fifth embedded in the hearth. The four upper electrodes are hung

from an overhead steel bridgework by means of steel cables fastened to counterweights. Vertical movement of the electrodes is accomplished by means of D. C. motors, which are geared to the counterweights. Regulation of the length of the arc is controlled by means of either hand controllers, or else automatically by means of a set of relays and contactors in connection with current transformers in the secondary leads to each electrode. A

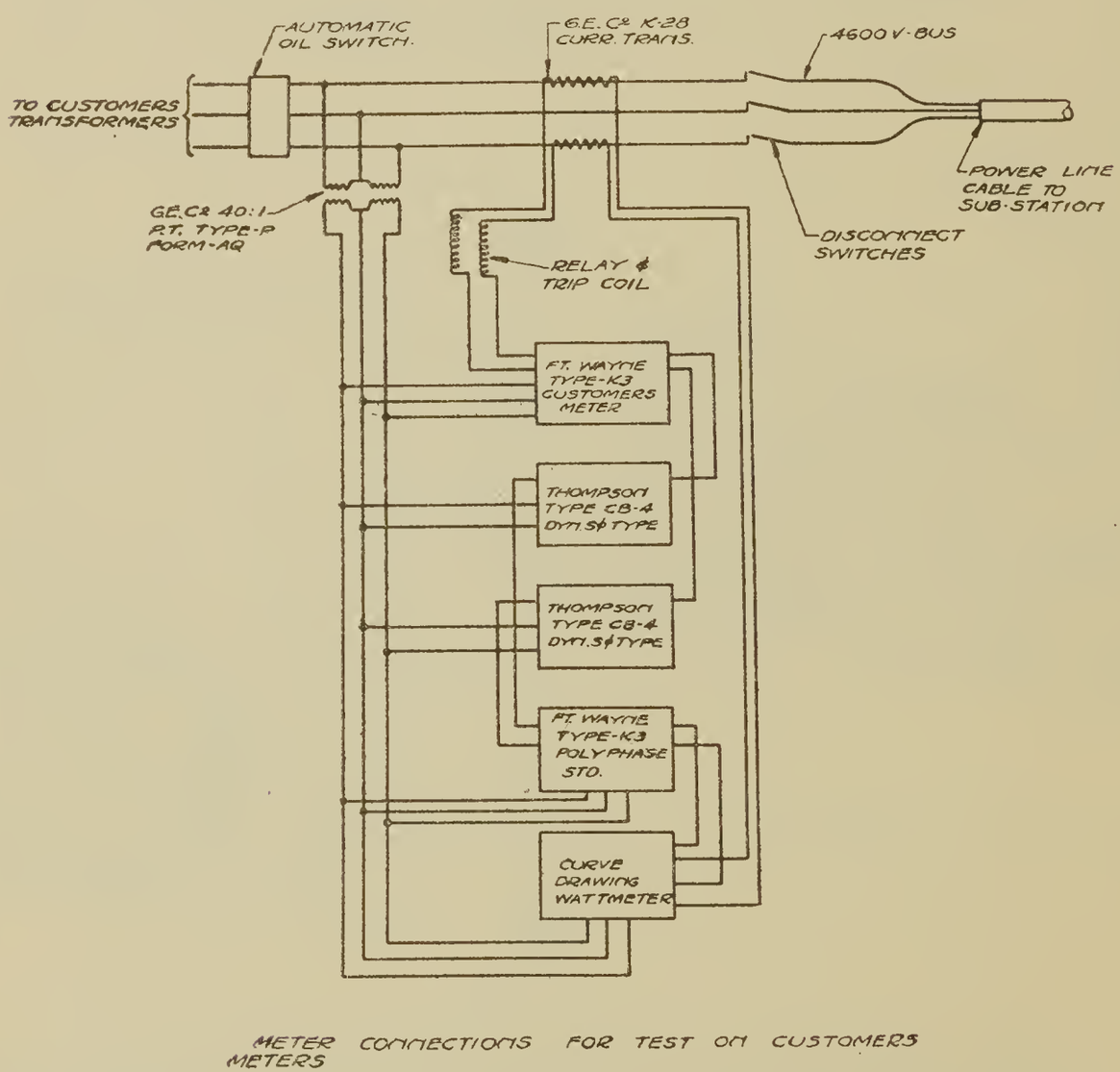

AUTOMATIC OIL SWITCH.
G.E. Co K-28 CURR. TRANS.
4600 V. BUS
TO CUSTOMERS TRANSFORMERS
POWER LINE CABLE TO SUB-STATION
G.E. Co 40:1 P.T. TYPE-P FORM-AQ
DISCONNECT SWITCHES
RELAY & TRIP COIL
FT. WAYNE TYPE-K3 CUSTOMERS METER
THOMPSON TYPE CB-4 DYN. S/ TYPE
THOMPSON TYPE CB-4 DYN. S/ TYPE
FT. WAYNE TYPE-K3 POLYPHASE STD.
CURVE DRAWING WATTMETER
METER CONNECTIONS FOR TEST ON CUSTOMERS METERS

FIG. 5.

feature of this regulation scheme is the gradual movement of the electrodes and the instant stopping at a desired point by dynamic braking of the motor. Either the manual control or the automatic regulation is effective at any one time and the control of any one of the four top electrodes is independent of the other three.

The furnace is rated at five-ton capacity, taking 1,200 K.W., two-phase energy. The four upper electrodes are connected in

pairs to two banks of Scott-connected, 3 to 2 phase, transformers. Each bank of transformers has its secondaries, 90° out of phase, connected solid without switches to the top electrodes. The bottom electrode furnishes the common return to each bank. By means of the switches on the primary side of the transformers, one bank with its electrodes may be placed either 180° or 120° out of phase with the other bank. Another distinguishing feature in the transformer connection is the arrangement, by means of primary taps, to vary the voltage at the electrodes. The voltage across the corresponding secondaries of one phase is either 90 or 60, according to the desired heat required in the furnace, being 90 V. for the 180° relation of electrodes and 60 V. for the 120° relation. This is controlled by the same switches mentioned above in the primary side. Connections from the transformer to the electrodes consist partly of solid bus bars and partly of flexible cables to allow for tilting of the furnace. The general scheme of connections is shown in Fig. 4.

The transformers are oil-insulated, self-cooled, with a maximum inherent reactance of 12 percent to each bank. The main transformer is rated at 300 K.W. and the teaser at 300 K.W. The transformers are energized from a three-phase, 4,600 V. bus, through the T.P.-D.T. switches which are hand-operated and non-automatic. A hand-operated automatic master switch is also cut in series in the main feed to guard against heavy overloads.

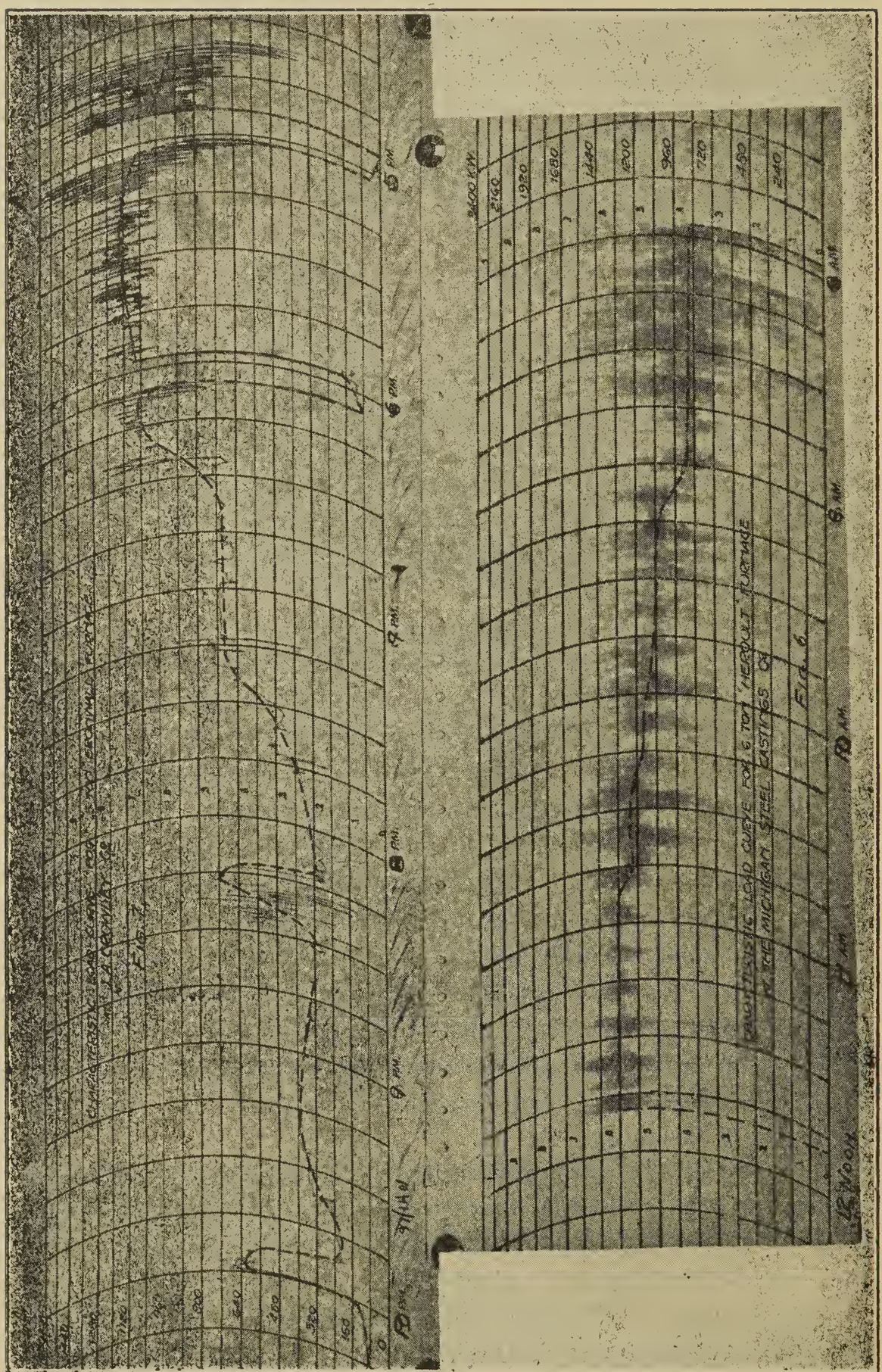
The metering is done on the primary side by means of a Fort Wayne, three-phase induction, type K-3, watt-hour meter connected to General Electric current and potential transformers, in the same manner as that described for the Heroult furnace.

The primary bus is fed by means of a 4,600 volt, 3 conductor, 200,000 c. m. (1 sq. cm.) cable, extending from the central-station bus, about 22,725 feet (6,930 m.) long, and feeding no other customers along its route.

For guidance in operating the furnace, indicating ammeters are installed in each electrode circuit, including the neutral. These are connected to General Electric Co. current transformers.

Operation of Furnaces.

The Heroult furnace is used to produce steel of variable carbon content as used in steel castings. With an acid lining, it is charged



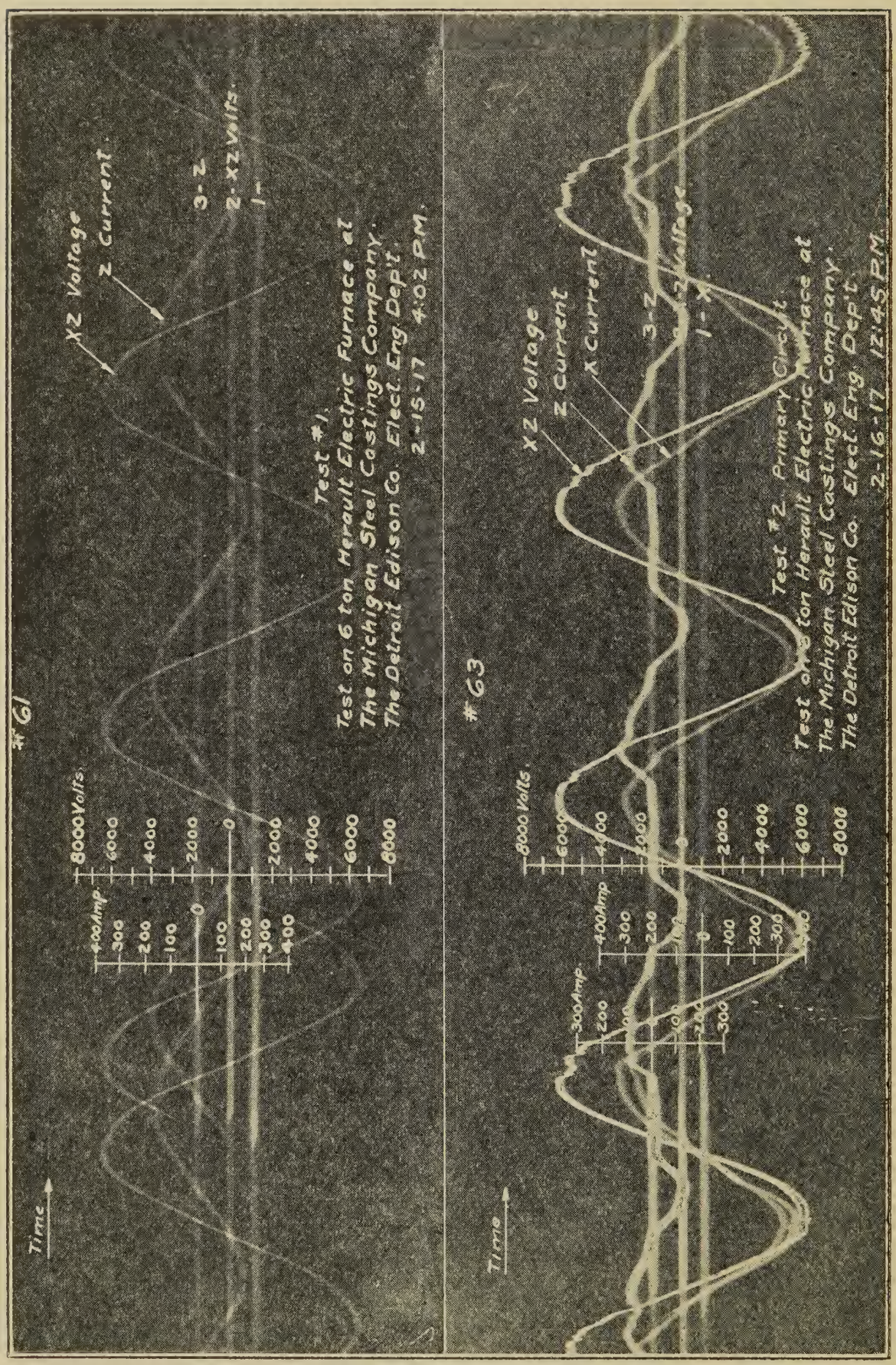
FIGS. 6 AND 7.

with steel scrap fairly low in phosphorus and sulphur and with some foundry scrap. Manual labor is used for charging, after which the current is turned on and the regulator adjusted for the desired current value. In the steel-castings trade there is not the necessity for extreme refining that is required in the alloy-steel manufacture, hence a heat may be finished more rapidly, and as a result the Michigan Steel Castings Co. is pouring five to six heats per day (24 hrs.) of about six tons each. A characteristic load-demand curve for the ordinary operation of this furnace is shown in Fig. 6. It will be noted from this that the average K.W. demand rises from about 750 K.W. at the start to about 1,300 K.W. at the finish of one melt.

The Grönwall furnace is used to produce high-grade alloy steels. With its basic lining it is charged with a scrap steel of all descriptions and of comparative low value. The furnace is charged by manual labor, after which the 60-volt current is turned on for a short time to start a pool of molten metal around each electrode. The transformers are then switched to the 90-volt connection and operated this way until all of the metal becomes molten, after which the connection is changed back to the 60 volt and held during the entire refining stage. The time for refining varies widely according to the kind of alloy steel wanted. Normally, under ordinary conditions, three to four heats are run daily, averaging about five tons each. A characteristic load-demand curve for normal operation during one heat is shown in Fig. 7. This curve shows a higher average K.W. demand at the start and a dropping off to a much lower demand at the finish than is the case with the Heroult furnace mentioned above.

Method of Testing and Results.

It was desired to study the load fluctuations and their consequent effect on the substation bus from which the cables feeding the furnaces emanated. For this purpose, curve-drawing instruments were installed and some of them speeded up at times in order to increase the time space on the chart. The curves, of course, were very irregular, especially during the melting down period, depending on the size and kind of metal used in charging. (Figs. 6 and 7 give a good idea of the fluctuations.) Although the current jumped to high values at times, the heating of the


#61
XZ Voltage
Z Current
3-Z
2-XZ Volts.
1-
Test #1.
Test on 6 ton Herault Electric Furnace at
The Michigan Steel Castings Company.
The Detroit Edison Co. Elect. Eng. Dept.
2-15-17 4:02 P.M.
8000 Volts.
6000
4000
2000
0
2000
4000
6000
8000
400 Amp
300
200
100
0
100
200
300
400
Time
#63
XZ Voltage
Z Current
X Current
3-Z
1-X
Test #2. Primary Circuit
Test on 6 ton Herault Electric Furnace at
The Michigan Steel Castings Company.
The Detroit Edison Co. Elect. Eng. Dept.
2-16-17 12:45 P.M.
8000 Volts.
6000
4000
2000
0
2000
4000
6000
8000
300 Amp
200
100
0
100
200
300
400
Time

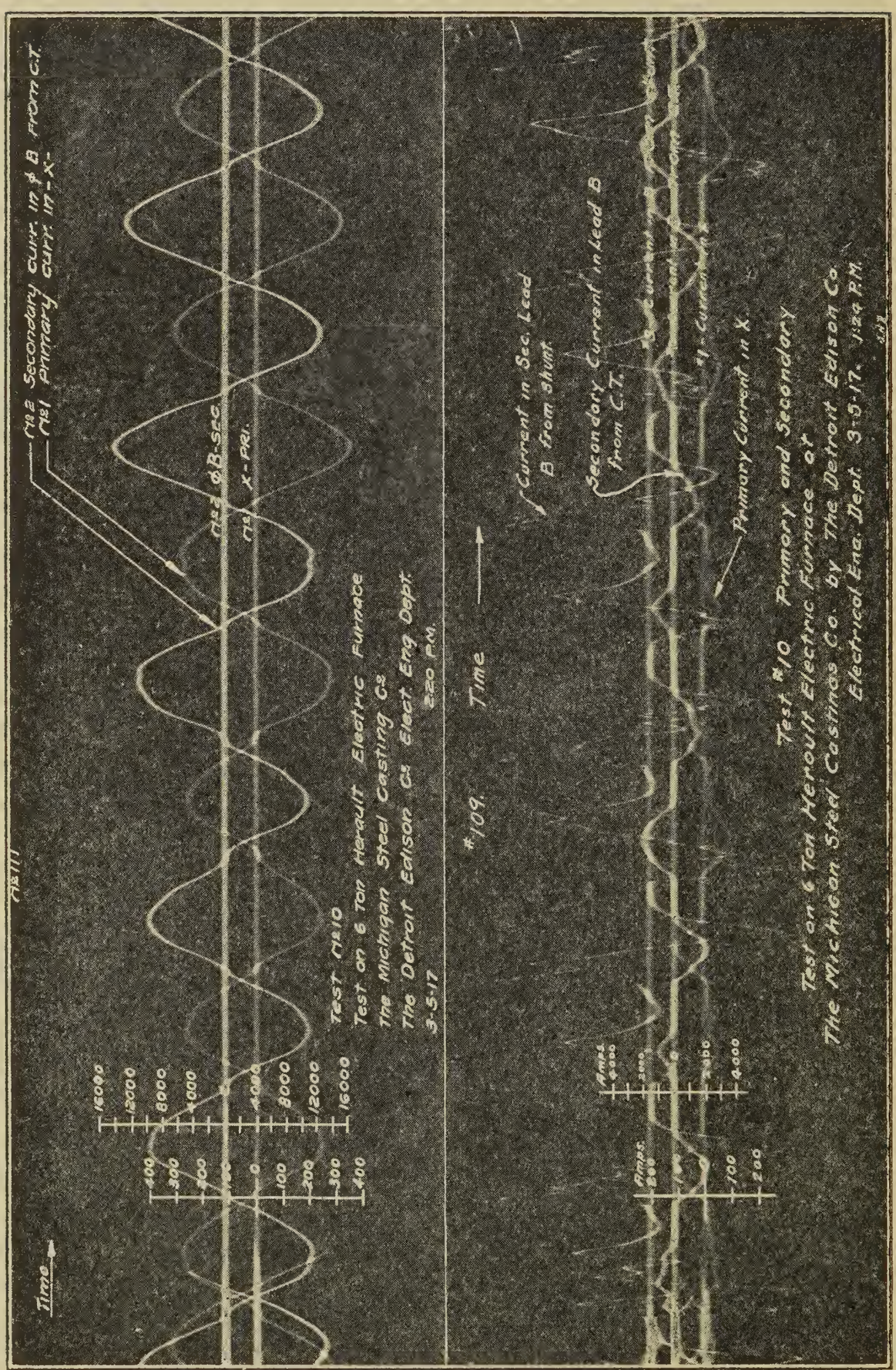
FIGS. 8 AND 9.

cables was insignificant and it did not cause worry at any time. The effect of the changing load on the bus pressure was not so serious as might be expected. With a considerable inherent reactance in the transformers and also the impedance in the cables, the pressure was found to vary on an average of 2 percent, the maximum being not over 5 percent from normal, and in general no ill effects were experienced in the substation. Power-factor readings were taken at the substation end with a power-factor indicator. The expression "power-factor," however, on an unbalanced three-phase load does not mean very much when we think of the load in its entirety. Nevertheless, it was desirable to get an idea of what the power factor might be and to consider the advisability of further investigation. From the readings obtained it was found that while the power factor went as low as 65 during the start of the melting down period, after 15 minutes the power factor came up to 85 very quickly, increasing to and remaining close around the 90 point during the refining period. But at no time during the operation was the power factor very steady. In view of the high power factor during the greater part of the operation, further attention was not paid to this phase. Power-factor readings which were taken at the customer's end of the line showed very nearly the same results.

To enable a better study of the load fluctuations, unbalancing and constant wave distortion, an oscillograph was made use of in the later tests. This was used at the substation ends of the cables feeding the furnaces and also at the customer's ends. The records obtained at the substation end during the range of one heat show in some instances some bad current wave distortions, especially during unbalancing of load. In severe unbalancing in the three phases, particularly during the melting down period, the current wave becomes slightly unsymmetrical. The potential wave, however, was not distorted appreciably at any time.

Tests on Customer's Premises.

Here, on the primary side of the main power transformer, several tests were run with the oscillograph, using the same current and potential transformers that were connected to the customer's watt-hour meter. Records were taken at frequent intervals during the same heat. Oscillogram No. 61 in Fig. 8 is typical of

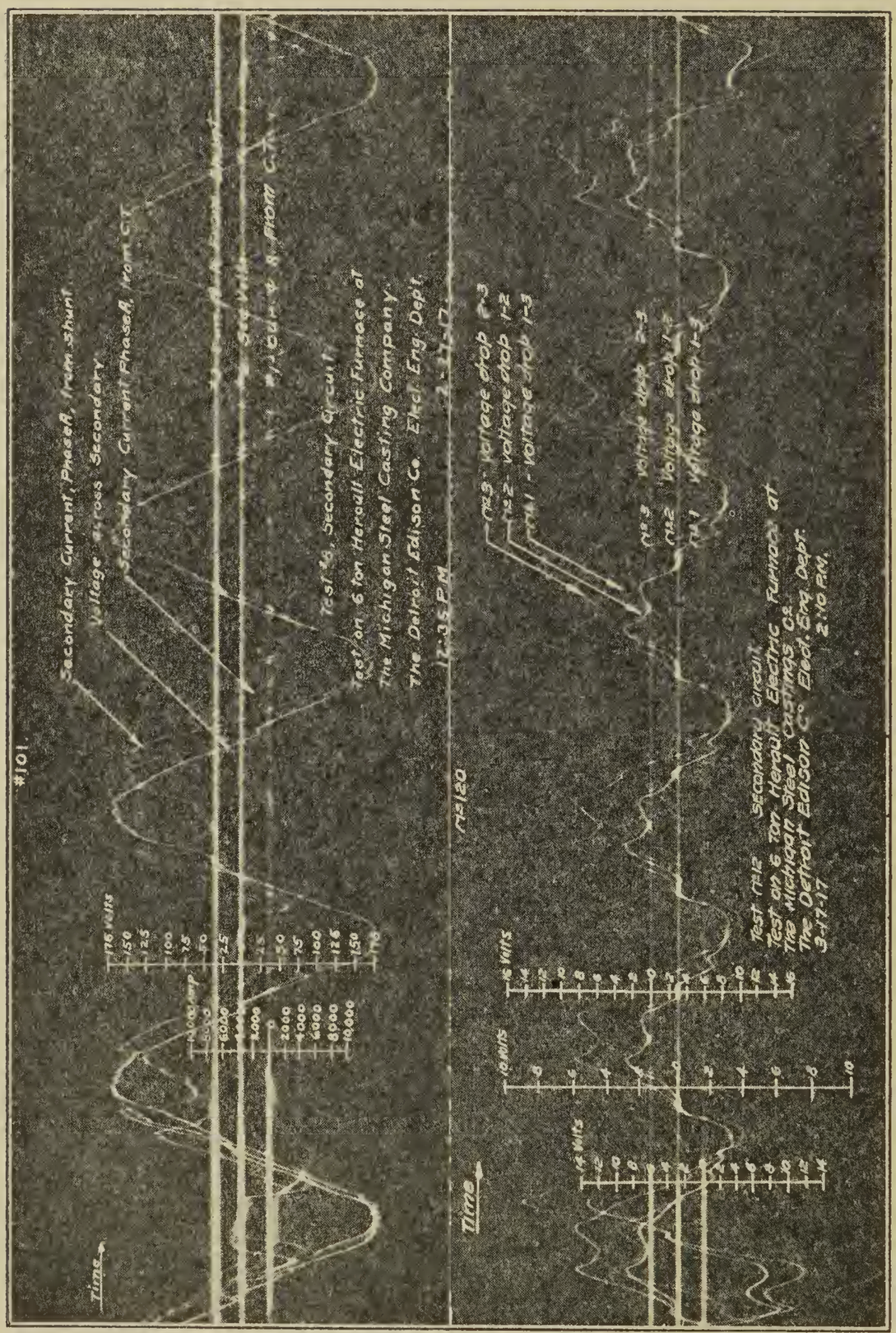

#2 Secondary Curr. in ϕ B from C.T.
#1 Primary Curr. in -X-
#2 ϕB-sec.
#1 X-Pri.
Test #10
Test on 6 Ton Heroult Electric Furnace
The Michigan Steel Casting Co.
The Detroit Edison Co. Elect. Eng. Dept.
3-5-17
2:20 P.M.
Time
#109
Current in Sec. Lead B from Shunt
Secondary Current in Lead B from C.T.
Primary Current in X
Test #10 Primary and Secondary
Test on 6 Ton Heroult Electric Furnace at
The Michigan Steel Castings Co. by The Detroit Edison Co.
Electrical Eng. Dept. 3-9-17. 1:22 P.M.

FIGS. 10 AND 11.

stable conditions, and oscillogram No. 63 in Fig. 9 is an example when the fluctuations were more violent. As a rule the curves show a greater distortion of both the current and potential waves at the customer's end than at the station end, which indicates a dampening out owing to the impedance of the cable. In the distorted current waves the third and fifth harmonics were frequently quite evident, and at times even harmonics appeared to cause an unsymmetry in the two halves of a wave. The voltage wave, however, in general was not far from a sine wave, except in some cases of bad current distortions. When the current waves showed sudden changes, the potential waves indicated high frequency disturbances of small magnitude, giving the potential fundamental a sort of saw-tooth appearance at or near the peak point. This is shown in oscillogram No. 63 of Fig. 9.

Another series of tests was run with the oscillograph on the secondary side of the power transformer. The distortions of current waves obtained by means of the current transformers were not far different than those obtained on the primary side. To make a better comparison of the primary and secondary currents, simultaneous readings of currents in the primary and in the secondary in the same corresponding phases were taken. Records of these are shown in oscillogram No. 111, Fig. 10, and also in oscillogram No. 109 in Fig. 11. It is surprising to note the similarity between curves 1 and 2 in both No. 109 and No. 111, in having the same corresponding distortions and the same unsymmetry. The inference might be drawn that the secondary wave shape is reflected through the power transformer and into the primary almost perfectly and without any so-called "dampening out" effect on the part of the power transformer, assuming of course that the current transformers used to get these results are correct. However, when we compare the actual values of current obtained in the secondaries of the two current transformers we find there is a small discrepancy. It appears also that the current transformers are not reproducing exactly in their secondaries the current flowing through their primaries.

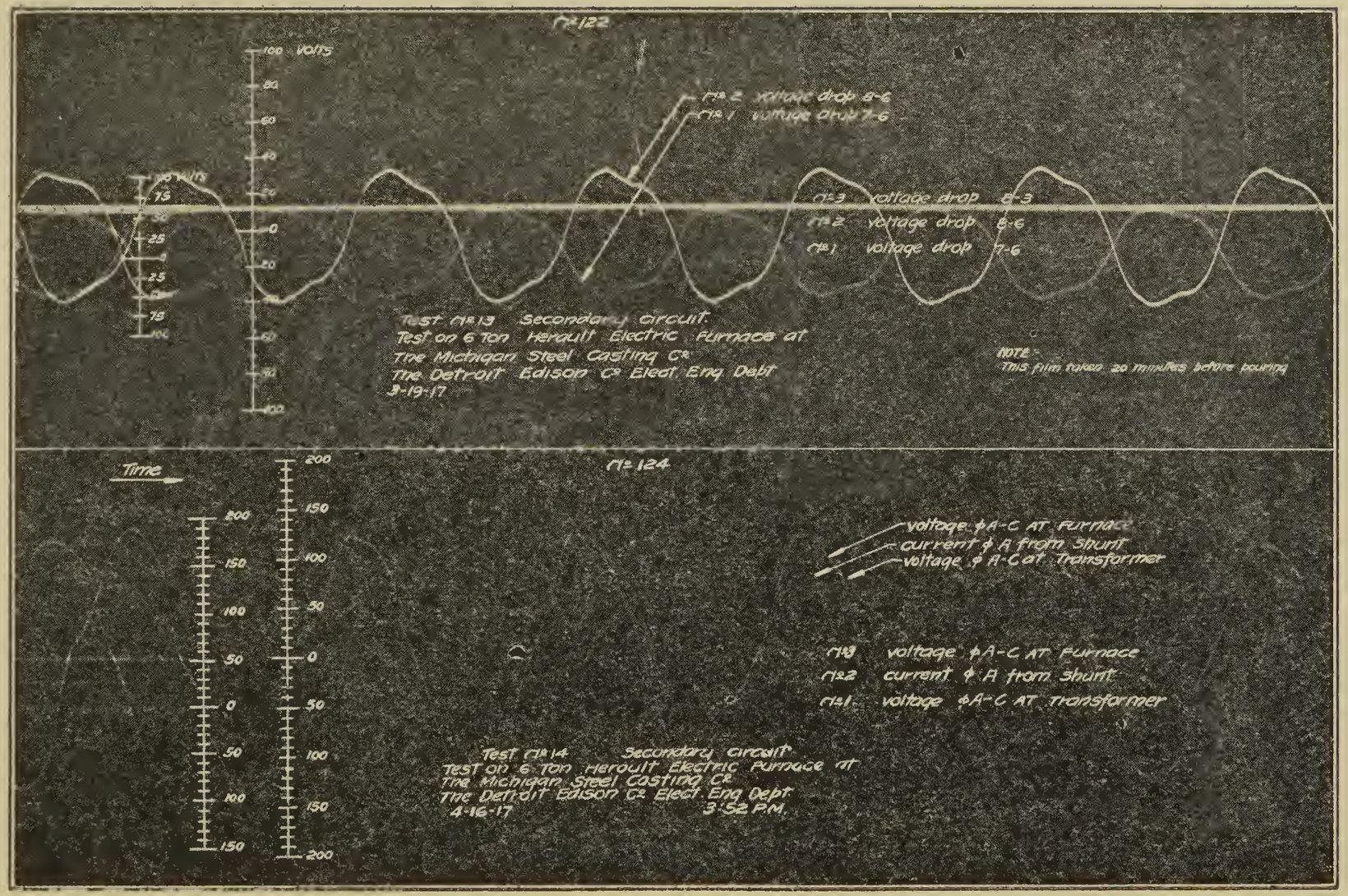
So far, all oscillograms were obtained by means of current and potential transformers. To study the nature of the current in the secondaries of the power transformers more directly, that is without introducing current transformers, the oscillograph was


#101.
Secondary Current, Phase R, from Shunt.
Voltage across Secondary.
Secondary Current Phase R from CT.
Test #6, Secondary Circuit
Test on 6 ton Heroult Electric Furnace at
The Michigan Steel Casting Company.
The Detroit Edison Co. Elect. Eng. Dept.
12:35 P.M.
Time
R3:120
R3 Voltage drop R-3
R2 Voltage drop R-2
R1 Voltage drop R-1
Test R12 Secondary Circuit
Test on 6 ton Heroult Electric Furnace at
The Michigan Steel Castings Co.
The Detroit Edison Co. Elect. Eng. Dept.
3-17-17
2:10 P.M.

FIGS. 12 AND 13.

connected directly to points selected on the main bus leads going to the electrodes. The potential drop between any two points (as *e. g.*, 1 and 4 in Fig. 3) on the same phase, would give an indication of the current flowing in this phase, its magnitude as well as its direction. Records (109 and 101 in Figs. 11 and 12) show the current derived by two methods, one the shunt method (curve No. 3) as just described, and the other by means of current transformers (curve No. 1), both being taken simultaneously. There is a surprising difference by the two methods. The shunt method gave current waves much more jagged and very little in common, except in the fundamental, with the waves obtained by the current transformers. This indicated that there was a large error and a dampening out of the current distortions in the electrode circuits by the current transformers. Another noteworthy point in connection with curve No. 1 in oscillograms Nos. 101 and 109 is the double peak formations in the current wave with a depression between them on each half of the fundamental wave. The peaks and depressions were undoubtedly due to the combined effect of the third and fifth harmonics, which together appear to be almost equal in amplitude to the fundamental. The frequency of the fundamental is of course 60 cycles, and its time space may be estimated from the corresponding time space of the secondary voltage curve (60 cycle) No. 2 of oscillogram No. 101. In addition to the third and fifth harmonics in the current wave, there were many unknown higher harmonics, as exemplified in the sawtooth fluctuations of curve No. 1 in oscillograms Nos. 101 and 109. Incidentally also, it will be noted in oscillogram No. 101 that there is a time lag in the current, as obtained by the current transformers, behind that by the shunt method. This is not, at the present writing, accounted for satisfactorily.

Next, a few readings were taken of the voltage drop over the various portions of the bus leads to the electrodes and also of the drop across the arc itself. Starting at the transformer and passing over the bus toward the electrodes, the points selected are designated as points 7, 1, 4, 2, 3, 8, and 6, in Fig. 3. Oscillograms Nos. 120, 122 and 124, in Figs. 13, 14 and 15, were obtained. It was found that of the total voltage available at the transformers as high as 24 percent was lost as drop in the copper bus between



FIGS. 14 AND 15.

the transformer and the electrodes, the balance being available at the arc. This seems like a large bus drop and is due not so much to the copper resistance as to the reactance of the bus circuit. To determine in what portion of the bus the greatest drop occurred, measurements were taken between points 1 and 2, in Fig. 3, and compared with those between 2 and 3, and it was found that the drop per c. m.-foot in the solid bus was over three times as great as in the flexible leads. Now, on account of the large cross-section of the bus to handle the large currents, skin effect may be a big factor in reducing the conductivity of the present bus, but it is believed that the induction of the neighboring steel work is largely responsible for the greater drop in the bus bars. On account of the necessary steel work giving support to the busses and the electrodes and its close proximity and unequal exposure to the different phases, considerable induction is introduced which cannot be easily avoided.

Besides the above-mentioned oscillograph tests, a few preliminary tests of interest were made with an ordinary direct-current shunt and an astatic ammeter. The shunt was connected in each electrode circuit of the Grönwall furnace, and in each circuit an apparent direct current was observed. In the neutral circuit a value as high as 3,600 A. was obtained. The direct-current indications were unstable but appeared to fluctuate proportionately with the alternating current values as obtained by the current transformer in the same phase. The apparent direct current in the neutral seemed to be about 70 to 80 percent of the total current indicated by the current transformer ammeter. It was also found that the polarity of this apparent direct current would reverse. The reversal, however, was not connected with any particular condition or change in conditions. There is probably some difference in opinion as to whether this is direct current, due to rectification, or whether it is not practically all alternating current, the ammeter merely giving the sum of the average values of the two halves of an unsymmetrical alternating current whose summation is not zero. That it should be such a large percentage of the alternating current which was indicated by the current transformer is surprising and worthy of further investigation with an oscillograph.

Meter Accuracy.

The last series of tests to be taken up and the most important, perhaps, concerns the accuracy of the watt-hour meter on which the energy charges are based. This is a Fort Wayne induction, type K-3, 3 amp., 110 volt, 60-cycle polyphase meter. Owing to the abnormal current wave shapes as obtained in the oscillograms, they being far from sine curves and also unsymmetrical with respect to the zero line at times, the accuracy of the meter was looked upon with suspicion. In view of the conditions it was decided to make such tests on the meter as was deemed advisable. Simultaneously with the meter tests, oscillograms were taken to ascertain the electrical conditions in the furnace.

Indicating instruments which were at first used did not give any valuable data for comparison and therefore watt-hour meters were used and readings were taken over a given period of observation. General Electric Co. Thomson (dynamometer type) watt-hour meters, properly lagged for low-power factor, were selected as standards, it being assumed that they are theoretically correct on any wave form. Two Thomson, type CB-4 rotating standards (portable watt-hour meters), were used to measure the three-phase energy output by the two-meter method and a Fort Wayne, type K-3, polyphase induction type rotating standard was connected in for another check. The readings of these instruments, together with the customer's meter, were compared against the dynamometer type, which was considered as theoretically correct. A curve drawing watt-meter was also installed to give indication of the load demands during any given period. Fig. 5 shows the various watt-meters used and their respective connections. The special registers of the rotating standards permitted short period runs to be read with high accuracy. Several runs were made during one heat and readings obtained during different conditions of the furnace operation. The results obtained in this manner were summarized and the average accuracy plotted in a curve.

In all of the tests, including both furnaces, the average error of the customer's meter was only 0.7 percent fast, the errors in any one run varying between 2.7 percent slow to 2.7 percent fast. This was all on the assumption that the dynamometer meters were correct and several preliminary laboratory tests on distorted waves indicated they were. The conclusions from these tests are that the meters at least are correct.

The results thus obtained, however, apply only to the meters themselves, and in view of the current transformers which were used and also their behavior as indicated in previous tests, the accuracy of the current transformers was questioned. The matter was then brought to the attention of the Electrical Testing Laboratories for further tests to determine the behavior of current transformers under distorted current wave conditions. Their finding was that a distorted wave in the primary of a current transformer was reflected almost perfectly through the current transformer and into the secondary under ordinary conditions of distortions. In view of the possible rectifying action of any arc furnace and the probable existence of direct current in the electrode circuits, a study of current transformer accuracy was made with direct current superposed upon the alternating current impressed on the primary of the current transformer, and it was found that the current transformer ratio was very materially affected by the presence of direct current. However, since in the customer's installation the metering was done on the primary side of the power transformer where no direct current is conceived to be existing, it was assumed that the meter current transformers were subjected only to the alternating current fluctuations and consequently, in view of the Electrical Testing Laboratory tests, indicated with a true ratio. This might be an easy and happy conclusion. However, there is still an element of doubt concerning such metering, especially after making a close study of some of the oscillograms, Nos. 109 and 101 in particular, in Figs. 11 and 12 respectively. Curves No. 3 were obtained directly from the bus without current transformers and in these there may be some direct current, but its apparent value is relatively small in both oscillograms. The distortions are certainly violent and appear to include, besides the fundamental, several of the higher odd harmonics, also some even harmonics or possible direct current, but the latter to a very small extent. The current transformers that were used do not seem to recognize these fluctuations and do not reflect them into their secondary circuits to any great degree of similarity, as shown by a comparison of curves Nos. 1 and 3. The question also arises: what happens to these distortions upon going through the power transformers? We have reason to believe that they do exist, being reflected through the large power

transformer, into the primary, perhaps somewhat "dampened out," and where the current transformers again do not recognize them. The nature of the possible current distortions in the primary is to be investigated in the near future with an oscillograph connected directly to the primary bus without current transformers.

SUMMARY AND CONCLUSIONS.

Investigations set forth in this paper have been the outgrowth of some preliminary investigations made at the furnace with some indicating ammeters and a power-factor indicator. The rapid and wide fluctuations of load, the heavy unbalancing of the different phases and the indication of direct current, presented problems beyond the scope of the ordinary indicating instruments and which could be better studied with an oscillograph. This was therefore brought in for further tests and when some of the oscillograph records revealed heavy phase unbalancing and some badly distorted current waves, the accuracy of the customer's watt-hour meter (induction type) on the service board was questioned. With such problems before us, several series of tests were made in which the oscillograph furnished some very interesting data.

In the first tests conducted at the substation end, no ill effects on the substation bus came to our notice. The fluctuations were rapid and badly unbalanced, yet the effect on the bus loading and on the bus pressure, with a large generator capacity connected, was not so serious as might be expected. Oscillograph records obtained showed that the current and potential waves were distorted inappreciably. The average power factor was good and usually much better than that of the average induction motor load on the system. Although it went down as low as 65 percent during the first few minutes of starting to melt, it soon reached 85 percent and then hovered close to the 90 percent point during the refining stage of each heat.

At the customer's end the wave distortions on the primary were a little more noticeable, indicating that the cable impedance was responsible for some "dampening-out" effect. This line impedance is desirable for various reasons, and without it the advisability of having either high transformer reactance or inserting external reactance, should not be lost sight of before taking on a new service to any electric furnace.

On examining the various oscillograms taken at the customer's end, it was found that the loading of the electrodes is far from being balanced at times, especially during the period when cold scrap is being melted. The melting scrap moves or collapses and the electrode circuits are interrupted or overloaded suddenly, causing an unbalance. This unbalancing, and the irregularities of load in the electrodes, constitute the chief factors in distorting the current wave out of its normal sine wave shape. Higher harmonics are also induced, such as the third and fifth and which are characteristic of the electric furnace, and their importance is not to be disregarded, especially in view of some of the data obtained in oscillograms Nos. 101 and 109, in Figs. 12 and 11 respectively. In many of the records there is also some indication of rectification or even harmonics causing unsymmetry of the two halves of the current cycle. The extent of this, however, in the observations made so far, appears to be relatively small and less than might be expected from an arcing furnace. The possible existence of direct current in the electrode circuits was brought to our attention in the tests conducted on the Grönwall furnace. The indications of the direct-current ammeter connected to a shunt in the neutral circuit were of surprisingly high value and varied proportionately with the alternating-current ammeter connected to a current transformer. Whether the indication of the direct-current ammeter is direct evidence of rectification is a matter in which there may be a difference of opinion. The direct-current ammeter merely gives the sum of the average values of the two halves of the current wave in a cycle, and in the tests indicated that it was not zero. In one of the tests the direction of the current reversed and we may argue that rectification as indicated by an ammeter is more apparent than real. While the oscillograms do not show a steady unidirectional current, yet the effect of direct current in distorting the current wave and causing unsymmetry cannot be denied.

The primary voltage wave was found to be, as a rule, only slightly distorted and no ill effect from it seemed probable, but because of the more serious distortions found in the primary current wave, suspicion arose concerning the effect of such distortion on the induction type watt-hour meter which is used to integrate the customer's load. The tests conducted so far have revealed

no appreciable errors and the first conclusion reached was that the meters were correct. As a matter of fact, however, there is still an element of doubt in the matter of correct metering, owing to the behavior of current transformers on which the meters depend, as seen from the oscillograms Nos. 101 and 109. It appears that the current transformers may not be performing their function in strict accord to what is expected of them, although some preliminary tests show that the meter current transformers should, in the position they are installed, indicate with a true ratio. It is the present intention to conduct further tests along this line of investigation, and it is hoped that such disputable but important points will be clarified in the near future. It should be noted that the meters in the present instances of metering are in the primary supply and that if they were in the secondaries of the power transformers, big errors would probably be introduced due to the evidence of the current transformers in the secondaries not reproducing exactly the currents existing in these circuits.

Attention was called in this paper to the large voltage drop in the secondary busses going to the electrodes. It was found that about 24 percent of the available voltage at the transformer was lost as drop in the short bus between the transformer and electrodes. This was unquestionably due not to resistance but to reactance which was introduced in the circuit by the neighboring steel structure of the furnace. Tests along various sections on this bus showed that the drop per c. m.-foot in the bus going through the steel structure, and with a current density of about 1.3 A. per 1,000 c. m. (0.05 sq. cm.) was over three times that in the flexible bus leads more remote from the steel work and where the current density was about 1.7 A. per 1,000 c. m. (0.05 sq. cm.). (See oscillogram No. 120, of Fig. 13.) The desirability of such reactance is a matter somewhat in dispute. On the one hand, the value of such reactance is claimed in its effect to cut down or limit sudden rushes of large currents. It should tend to smooth out the sharp peaks. However, it does not appear to have such great effect in the oscillograms of Figs. 11 and 12. On the other hand, reactance in such a place is detrimental to the voltage regulation and causes a big reduction in the voltage available at the arc. It is of course primarily due to the bus bars passing through or in close proximity to the steelwork. Its magnitude cannot be

easily evaluated because of so many unknown factors, and consequently little attention is sometimes paid to it in designing furnace installations. In view of its usually unknown value and the heavy currents to be dealt with in furnace work, it would seem more desirable to reduce it to a minimum and figure on a more definitely known inherent reactance to be incorporated in the power transformers. Closed magnetic circuits around or near any of the electrode circuits are objectionable for various reasons and should be avoided as much as possible.

In conclusion the author wishes to point out that the data and deductions as presented in this paper are not above criticism. The work was entirely new, much of it being performed under adverse conditions and not with as highly refined methods as now seem possible. The data obtained, however, looked so interesting that they were considered, even in an incomplete form, worth presentation at this time. It is hoped that the subject matter will invite criticism and also induce further investigations. It is the present intention to continue the work and possibly repeat some of the tests, in hopes that some of the disputable and unsettled points, particularly the meter accuracy, will be clarified.

The author wishes also to take this opportunity to express his thanks to Prof. T. J. MacKavanagh, of the University of Michigan, and Mr. J. Gilmartin, Superintendent of the Meter Department of the Detroit Edison Company, for the assistance given in making the investigations. Prof. MacKavanagh assisted in conducting several of the tests and also gave valuable advice in interpreting some of the results obtained in the oscillograms. Mr. Gilmartin supervised all of the meter tests and determined the accuracy of their results.

DISCUSSION.

H. M. St. John[1]: I think we can consider it definitely proved that we do get rectification in an arc furnace of this type. Three independent investigations have shown that. There need be no surprise that the rectification appears to reverse in direction, because such a rectifier as we have under these conditions is of the

[1] Research Engineer, Commonwealth Edison Co., Chicago.

contact type, and contact rectifiers are notably eccentric, frequently reversing the direction of their operation without apparent cause.

There is another point in that connection which has been of especial interest in the case of the single-phase, single-electrode furnace, and that is what part rectification may play in the low power-factor of such a furnace.

The point has been made, and there is some experimental evidence to back it up, that the low power-factor of the single-phase, single-electrode furnace is largely due to the rectification which occurs in the arc; but at the same time it has been brought out that the rectification is very eccentric, does not seem to vary uniformly with any of the other furnace conditions, and does reverse in direction.

Our experience in Chicago with several of these furnaces, some working on steel and some on bearing-bronze, does not seem to bear this out. We have found that there is a practically constant relationship between the arc voltage and the power-factor, for a definite reactance in the furnace circuit. With 220 volts no-load voltage and 150 volts normal operating voltage, these furnaces show practically a straight line relation for power-factor plotted against arc voltage throughout the range from 100 to 160 volts. At about 160 volts the graph appears to break, and the improvement in power-factor with increased arc voltage becomes less marked.

It hardly seems probable that if the rectification had any great effect on the power-factor, the latter could vary uniformly with the arc voltage, since the rectification certainly does not vary in any such manner.

It is important to know whether the power-factor of such a furnace can be improved by reducing the impressed voltage, and at the same time reducing the impressed reactance, since the shorter arc would not require so much reactance for its stabilization. Under these conditions the furnace would still show rectification, and if this is the primary cause of the low power-factor no improvement would result. If, on the other hand, the low power-factor is due to the effect of the high reactance required to stabilize the long arc, a reduction of the impressed voltage will have the desired effect.

J. A. SEEDE[2]: I think it should be a matter of record for Mr. Meyer to state the kind of slag used in the furnace when the tests were made. Mr. C. A. Hansen made some similar tests a few years ago, and found there was a considerable difference in the shape of the current wave, depending on the kind of slag used at the time the readings were taken.

A. A. MEYER: I do not believe I can answer that question. I cannot say what kind of slag there was during the various tests. Perhaps Prof. MacKavanagh can give us some information on that point.

T. J. MACKAVANAGH[3]: Regarding the effect of rectification on the power-factor of the furnace, we have not considered rectification important in this investigation. In dealing with a three-phase furnace, it is well to remember that even when the load is non-inductive, if the phases are unbalanced the power-factor of the system is not unity. In our case, the power-factor of the load, observed at the primary terminals of the transformer, varied from 65 to 95 percent, the low power-factor synchronizing with overload during melting down and unbalancing of the phases.

In the very earliest investigations on the A. C. arc, in which carbon electrodes were used, it was observed that the shape of the electrodes, and temperature variations due to the drafts, affected the wave shape of the current, and the power-factor of the arc.

Electrode material, magneto-motive forces not due to the current in the arc, and gases introduced into the arc, affect wave shape, rectification and power-factor.

The furnace slag generally exhibits electrolytic conduction; and it is quite probable that they can be investigated in the research laboratory, their electrical characteristics determined, and their influence on furnace operation forecast without recourse to tests on furnaces in the works, where everything seems to be against accurate determinations.

When we are ready for the last word on rectification, I quite expect to hear that its effect on the power-factor of the furnace is negligible.

[2] Electrical Engineer, General Electric Co., Schenectady.
[3] Asst. Professor of Electrical Engineering, University of Michigan.

J. L. DIXON[4]: I was present when some of Mr. Meyer's tests were going on, and one particular test I remember. The engineers at the test told me that the direct current was reversing itself, and I happened to notice particularly just at that time that the slag was becoming completely reduced, and turning white.

ROBERT TURNBULL[5]: Are we to understand that oscillograms were taken during the refining period, or the melting period?

A. A. MEYER: At various periods, at the very start of throwing the current on the cold charge, after a small pool of metal was formed, after all metal was melted, during the refining stage and just before pouring. We continued taking oscillograms through a complete cycle of furnace operation. The most violent distortions, of course, came during the melting down. During the refining period the curves were sine waves, or nearly so.

PRESIDENT FITZGERALD[6]: What furnace were Hansen's experiments done on, single-phase or three-phase furnace?

J. A. SEEDE: Three-phase, with transformers connected open delta.

S. L. BEAR[7]: I would like to ask Mr. Meyer what type of shunt was used in the secondary of the transformer.

A. A. MEYER: We could not get a shunt big enough to go in series and carry the whole load, so we used a portion of the bus load itself as a shunt and ran the wires from that to the oscillograph.

S. L. BEAR: I believe the current measured in that way would not be a true representation of the current in the bus-bar, owing to the reactive drop in the bus-bar.

A. A. MEYER: Of course we did not have a non-inductive shunt and our current values obtained from the shunt may not be exactly correct, but this method gave a fair idea, I believe, of the fluctuations occurring in the electrode circuit.

S. L. BEAR: I notice that the oscillogram obtained by means of the shunt is apparently 90° out of phase with the current in the furnace leads.

[4] Chief Engineer, J. A. Crowley Co., Detroit.
[5] Maker of Electrode Regulators, Volta Mfg. Co., Welland, Canada.
[6] FitzGerald Laboratories, Niagara Falls.
[7] General Engineer, Westinghouse Electric & Mfg. Co., East Pittsburgh.

A. A. MEYER: It was not 90°, it was 60°, or nearly so, in some cases a little bit less. We have not yet arrived at a satisfactory explanation for that.

S. L. BEAR: Would not the higher harmonics in the current of the furnace circuit cause a rather bad distortion of the wave obtained by means of the bus-bar shunt?

A. A. MEYER: You would probably expect it, but the distortions are also evident from the current transformer as seen in curves 1 and 2 of oscillogram No. 109. You can easily pick out the fundamental wave obtained by the shunt as being 60 cycle and closely related to the disturbance as indicated by the current transformers. Superimposed upon this fundamental are the high-frequency distortions.

S. L. BEAR: You stated, I believe, that the power-factor obtained was by means of a power-factor indicator.

A. A. MEYER: Yes.

S. L. BEAR: The power-factor meter indicates the phase difference between the fundamentals of voltage and current, but that indication is not the true power-factor in case either the voltage or current waves contain higher harmonics.

A. A. MEYER: That is true. Three-phase power-factor readings, however, do not mean much in case of a heavily unbalanced load.

S. L. BEAR: The true power-factor can be obtained by measuring the volts, amperes and watts of each phase. By means of this you can get the ratio of the kilowatts to the kilovolt amperes, and I believe the central station operators are principally interested in that ratio.

A. A. MEYER: Yes, there are several ways of getting power-factor. On account of the good average power-factor (around 95 percent) we were not seriously concerned in power-factor accuracy.

J. W. RICHARDS[8]: There is one consideration which may help to explain the shape of the wave. In the furnace at a high temperature, you have metallic vapors, such as those of iron, silicon

[8] Professor of Metallurgy, Lehigh University.

and manganese, and during the refining period perhaps also of calcium, from the slag. These metallic vapors tend to take away the arc characteristic of the wave, and give it rather the form of a resistance wave, that is, to suppress the little hump in the wave. That may possibly account for the change of shape when you have a heavy slag, and particularly during the refining period.

B. I. WHITING[9]: Metallic vapors in the furnace have much to do with the maintenance of the arc. An incident noted some time ago in the operation of a basic-lined single-phase, single-electrode furnace may be of interest. Under normal operation the voltage drop across the arc was about one hundred and thirty volts. At the time of tapping an extremely high temperature heat, the arc did not break when the electrode was raised from a position just above the slag to a position about eighteen inches higher. The slag was very fluid and basic, of course. It was some time after one door had been opened before the arc was broken.

The fact that the vapor apparently broke down along a different path at each succeeding alternation of the current was also noted.

J. R. CRAIGHEAD[10] (*Communicated*): Mr. Meyer shows in Figs. 11 and 12 the comparison of primary and secondary currents in a current transformer, where the current flowing through the primary is badly distorted. The oscillogram of secondary current shows a wave considerably out of phase with the primary, and most of the harmonics of the primary current are apparently absent from the secondary. It would be of interest if Mr. Meyer would explain the exact conditions under which the oscillograms were obtained, as the distortion appears much greater than is usually caused by current transformers, even when operating on badly distorted waves.

Some time ago the writer took similar records on a three-ton Snyder furnace used for melting steel scrap. The furnace was single-phase, using a single-electrode and having the return circuit through the charge and frame. The supply was from the teaser connection of a set of Scott-connected power transformers. Two of the records obtained are shown in the figures. In Fig. 16,

[9] Electric Furnace Engineer, Leavitt & Co., Agents for the Girod Furnace, New York City.

[10] Electrical Engineer, General Electric Co., Schenectady.

the lower curve shows the current through the furnace by recording the drop from a shunt, and the middle curve the same current as taken from the secondary of a current transformer. In Fig. 17 the order of the curve is reversed.

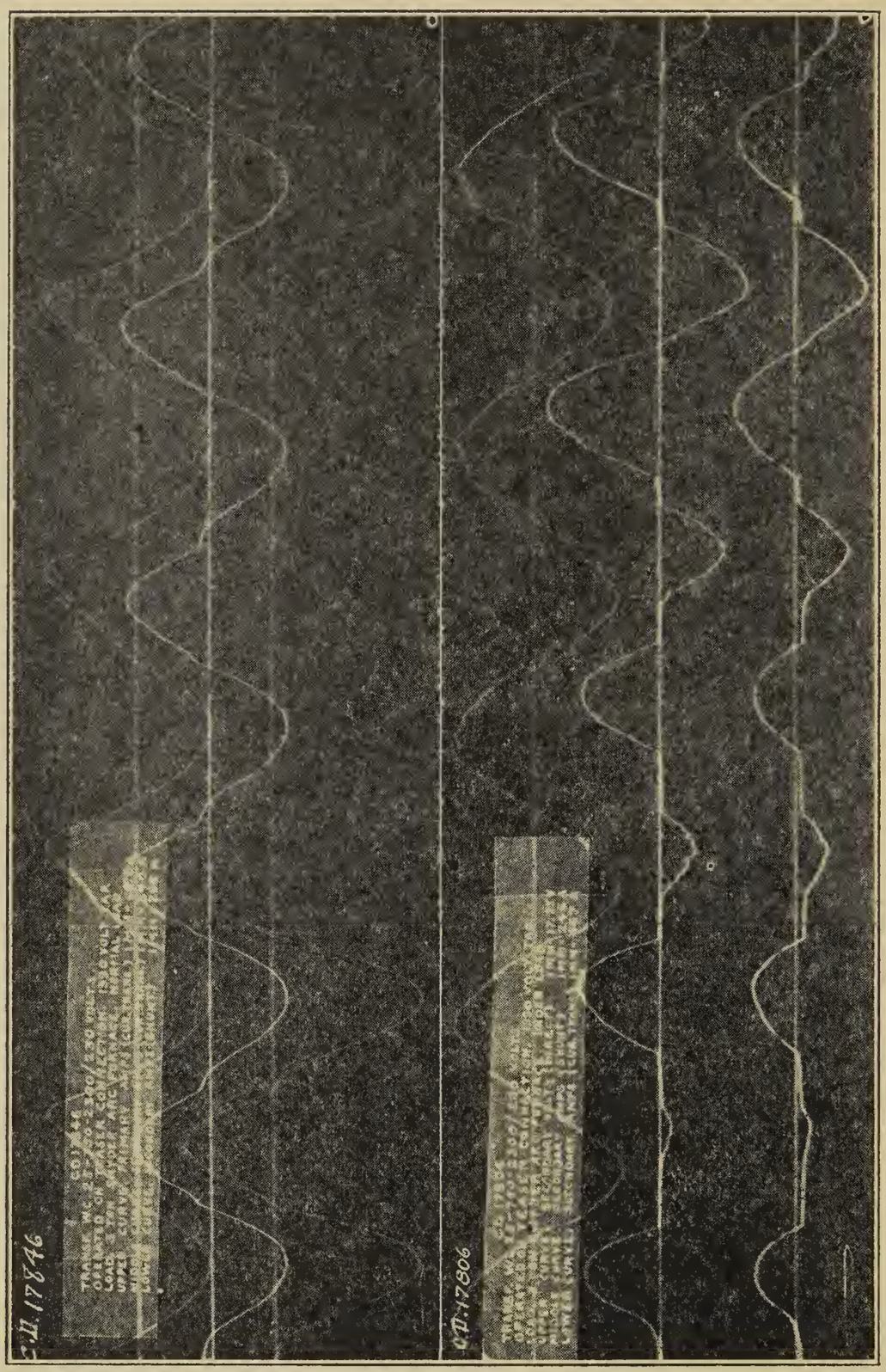
As the Snyder furnace has a single arc of several inches length, whose terminals are unlike (electrode and charge), considerable rectification is to be expected, and is shown in the curves by the greater average area of the half waves above the zero line than of those below. Fig. 16 shows a steady condition, while Fig. 17 shows nearly complete suppression of one half wave. In both cases the primary wave is quite closely duplicated in form and phase position in the secondary, but the entire curve is shifted across the zero line in a direction tending to equalize the areas of half-waves above and below the line. It will be noted that minor variations of the primary current are reproduced in the secondary with good accuracy.

The average value of the direct current was obtained by the use of a planimeter to integrate the difference between positive and negative areas for two cycles together. This difference was divided by the abscissa, and the resulting ordinate multiplied by the calibration value gives the average direct current component. In every case this component was greatly diminished or entirely suppressed in the wave obtained from the secondary current; where average areas for several cycles are considered, the D. C. component apparently disappears.

The following table shows the results, all values being given in terms of primary current:

	Average D. C. from Oscillograms		Current from A. C. Ammeter on
Figure	Primary	Secondary	Secondary
16.....	1575	0	4250
17.....	865	282	3200

It is evident that any D. C. component in the primary will not be represented in the secondary circuit. Further, the presence of this direct component in the primary winding will cause the transformer to operate through an unsymmetrical cycle of flux, with increased errors of ratio and phase angle. These errors cannot be corrected by allowance, as they change through considerable ranges with momentary change of conditions. On the other hand, if there is little or no rectified current, the current transformer



Currents in Primary and Secondary of Current Transformer. Fig. 16 and 17.

will reproduce distorted wave forms with good accuracy, adding very little to the other errors of metering.

Arc furnaces may therefore be divided into two general classes, with respect to the errors of metering due to current transformers. First, those in which each arc has a definite circuit in which its D. C. potential may operate to cause direct current, as in the Snyder furnace, and as shown in Mr. Meyer's diagram of the Grönwall. Here a considerable D. C. component is to be expected, especially if the arc is comparatively long, and accuracy of the current transformers will be poor. Second, those in which each complete furnace circuit contains two arcs, generating voltages in opposing directions, which partially neutralize each other, as shown in Mr. Meyer's diagram of the Heroult. Here the rectification is irregular in direction, and, especially with short arcs, small in amount except under starting conditions. Hence the errors in metering caused by current transformers will be comparatively small.

In both cases, however, more correct results would be obtained by metering on the primary side of the supply transformers, and this method should be preferred, unless it is important to separate the transformer losses from the energy consumed by the furnace.

A. A. MEYER: In answer to the question Mr. Craighead raises concerning the conditions under which oscillograms Nos. 109 and 101 were taken, I will state that both were obtained during the start of the melt. Referring to oscillogram No. 109, curve 1 was taken by means of a current transformer shown in X phase in Fig. 3. Curve 2 was taken by means of a current transformer shown in the B phase in Fig. 3. The 400 K.V.A. transformers (Fig. 3) were connected delta delta and the X primary phase corresponded to the B secondary phase (as determined by test). Curve 3 of oscillogram No. 109 was obtained by taking the drop along a portion of the bus in the B phase and between points like 1 and 4 of Fig. 3. Leads were carried direct from the current transformers and shunt to the three elements of the oscillograph. The currents 1 and 2 in oscillogram No. 109 are in phase, although shown 180° out of phase, but current No. 3 is considerably out of phase. In several other similar tests the phase displacement was about 60°. This is, as yet, not entirely explained, although

it is believed that the inductance of the shunt or bus lead between points 1 and 4 of Fig. 3 is largely responsible.

I might say that since the first writing further tests were conducted to determine the wave shape on the primary side of the power transformers. A standard D. C. shunt was connected in the primary lead phase X, Fig. 3, and the current determined by means of it compared to that by means of a current transformer in the same phase X. This was done during the operation of the furnace and the current wave shapes and values obtained by this method agreed so close that it seemed safe to conclude that the current transformers in the primary side of the power transformers were reproducing in their secondaries exactly the current distortions in their primaries, and that our present method of metering such furnace load on the primary side was correct without any appreciable error. The distortions existing in the secondaries of the power transformers, however, seemed to affect the current transformer accuracy and also appeared to be damped out by the power transformers. This suggests a possible error in metering furnace loads on the secondary side of power transformers.

Attention was called in the paper to the large voltage drop in the bus leads to the electrodes. The actual energy loss in these buses also came up and tests were conducted. From watt-hour tests it was found that of the total energy delivered to the furnace, about 5½ percent was lost in the bus leads. Here again the energy loss was not due so much to copper resistance, the latter being only 10 percent of the 5½, as it was due to hysteresis in the neighboring steel and eddy currents in the copper bus. The effect of the stranding in the flexible leads or cables to reduce eddy currents was also quite evident from our results. While 5½ percent loss is a comparatively small loss, yet as an operating charge in such size load it is worthy of consideration and every effort should be made in the design of new installations to reduce it to a reasonable minimum. Buses should be as short as possible and should be built up with due regard to skin effect and eddy current loss. They should be arranged to have a low value of self-induction. Closed magnetic circuits should be avoided and the desired or necessary reactance should be incorporated rather in the power transformers.

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LOW TEMPERATURE ELECTRO-THERMAL PROCESSES.

By C. F. Hirshfeld.*

[*Abstract.*]

A detailed description of the art of japanning, and how it has been found that electrical baking gives such exact control of temperature conditions that highly superior work is done in a shorter time. The baking of cores for foundry work was similarly studied, with the result that electrical baking is found to give far superior results. Suggestions are made as to other fields, in which low temperature electrical baking will certainly make a great improvement, such as the baking of foods, breakfast cereals, etc.

Those who have become familiar with the various uses of electric furnaces of one sort and another have come to recognize the fact that, in a general sense, the electric furnace can not be considered a commercial competitor of furnaces heated by combustion. The use of the electric furnace must make possible the attainment of something unattainable by combustion methods or else there is no possibility of its being used in place of the older type excepting, possibly, under very unusual conditions as to the relative costs of fuel and electrical energy.

If this is true of high-temperature processes such as are commonly associated with electric furnaces it needs no argument to prove it true for low-temperature processes in which combustion methods have a greater advantage on an energy cost basis, because of the lower temperatures at which the products of combustion can be discharged.

This condition is frankly admitted, and it should be understood at the start that it is not the intention of this paper to urge the

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general substitution of electric heating for combustion heating in low-temperature processes in general, or in some low-temperature processes exclusively. There are certain low-temperature processes which, under certain circumstances, can be conducted to better commercial advantage by means of electric heating than is possible by means of combustion heating, and it is the purpose of this paper to point out some of these processes, some of the phenomena connected therewith which indicate the advisability of heating electrically, and some of the possibilities which electric heating unfolds.

The term low temperature is not exact, but for present purposes may be taken as referring to temperatures below about 290° C. (554° F.). Such temperatures are below practically all commercial metal-melting temperatures but are common in numerous baking and drying operations which form a surprisingly large part of industrial processes.

The exploitation of electric heating for such low temperatures in industrial practice is really comparatively old, since numerous small electrically heated appliances operating at such temperatures have been used as a matter of convenience in manufacturing establishments for a number of years. During the past few years, however, the use of electric heating for such temperatures has been adopted in cases calling for the installation of equipments with capacities ranging from several hundred to several thousand kilowatts. This is obviously a different sort of a proposition, and must be based on a far broader consideration than mere convenience.

The best example of the extensive adoption of electric heating for low-temperature work is furnished by the electric japanning equipment installed during the past few years. For this reason this industry will be discussed at some length.

The name "japan" originally referred to a sort of liquid lacquer or varnish made from vegetable sources in Japan and used as a protective or decorative coating on objects made of wood and other materials. This original japan was converted into a hard, brilliant material by exposure to sunlight. At the present time the word japan is used as a sort of collective title for a number of paint-like materials which are intended to be baked at various temperatures between 100° C. (212° F.) and 260° C. (500° F.)

and which are generally used for decorative or protective coatings on metal objects.

Originally, these baking japans were much like varnishes to which pigment had been added, but as the development of the industry made more and more specific demands the number of japans manufactured was greatly increased and many different type formulas were adopted. At the present time one can purchase under the name "japan" materials varying all the way from combinations of pigments with driers, linseed oil and expensive gums to materials which are little more than Gilsonite or other asphaltic compound carried in a suitable solvent with enough oil or similar material to make it resilient after baking. Driers are often included in the mixture, but this is not a universal practice.

The changes which occur during the baking of these japans are very complicated, and are not yet entirely analyzed from the scientific standpoint. It is certain that the solvent partly or wholly evaporates during the baking, and it is also certain that the oils and gums undergo oxidation and polymerization. It is also probable that complicated reactions occur between the numerous varieties of hydrocarbons and hydrocarbon derivatives present in the mixture.

The general lack of exact knowledge is shown by the fact that few, if any, makers of japan can predict the behavior of their materials under unusual conditions.

At the present time a number of chemists who have been specially trained in the technology of paints and varnishes are at work on japans, and it is probable that more exact information with regard to these materials will be available in the future.

When electric baking of japan was first considered a few years ago, it was found that practically all japanning practice was of an empirical character. Moreover, no two japanners seemed to agree upon the proper methods of applying and baking a given japan even when all essential variables, such as weight and character of work, were the same. Discussion of the various problems with many users and with many makers of japans brought out the fact that practically all agreed upon certain rules and regulations but that there was a large mass of so-called trade secrets which were, partly or wholly, mutually contradictory.

Obviously, this particular art had not yet progressed beyond

the empirical state. Scientific analysis had not been extensively undertaken, no consistent mass of scientifically accurate facts had been accumulated, and operators were hired on the basis of a self-advertised collection of rules of thumb combined with most wonderful and weird imaginary charms of various sorts for insuring excellent results. The executives responsible for factory production were entirely at the mercy of these self-styled experts, some of whom were really remarkably clever men, but many of whom could lay no claim to such a title.

It is not surprising that, under such conditions, the japanning room should have been a source of constant worry. On one day very satisfactory results were obtained, and on the next all sorts of imperfections appeared.

In many establishments an average rejection of as much as 10 percent of the finished work was regarded as a characteristic of japanning processes and was taken as a matter of course. In some instances on record rejection of over 50 percent for several days in succession occurred at irregular intervals.

Such facts indicate plainly to the trained observer that one of two conditions exists. Either the conditions necessary to insure completely satisfactory work are not known or else the control of the essential variables is imperfect. In the case under discussion both conditions seemed to exist and the methods in vogue made it so impossible to control the essential variables that little opportunity existed for studying, in the field, the effects produced by giving them different values.

As an example of the complications to be met consider the possibilities existing in any given case. Assume, for instance, a given japan used in connection with a given piece of material.

1. The japan may be thinned to various degrees, but there must be some value which will give the most satisfactory flow combined with proper covering of the article.

2. The japan may be maintained at a number of different temperatures during application, but there must be some temperature which will give the best results.

3. The material being covered may have a number of different temperatures when the japan is applied, but there must be some best value.

4. The length of time during which the material is allowed to

drip or stand after the application of the japan may vary widely, but there must be some best time.

5. The temperature of the material and surrounding space during the interval between application and baking may have numerous constant or changing values, but there must be some best value.

6. The law of temperature rise during baking is capable of infinite variation, but there must be some best sequence of temperatures.

7. The law of temperature fall after the maximum baking temperature has been maintained for the requisite length of time is also capable of infinite variation, but there must be some best sequence.

8. The condition of the atmosphere, both with regard to contained moisture, contained japan vapors, and contained impurities or admixtures of various sorts, must have a decided effect and some best condition must be possible of attainment.

Admittedly the list of variables is formidable, but they are all of such character as to yield to simple experimental investigation. Unfortunately, the effects of practically all are overlapping, and a thorough investigation must therefore involve a great expenditure of time.

The application of electric heating to this art served the very useful purpose of making it possible to control accurately some of the variables, and the combination of electric heating with the continuous methods which were introduced with it made this control more extensive and automatic. With the combination of electric heating and continuous types of oven as now built, it is possible to control accurately and automatically all of the variables listed above. Therefore, if one piece of work is satisfactory all must be satisfactory, if they come to the japanning room in the same state of preparation and if they have the same characteristics as to quality of material, contour, distribution of mass, etc.

Much of the credit for the control attainable with electric heating must be given to the mobility of electric heating units. They can be shifted about with great ease until that particular arrangement which gives the best temperature distribution and best temperature gradient is discovered. After they are once located in such positions, the results attained are independent of all of the variables characteristic of combustion processes. Their perform-

ance must be the same not only day after day, but even year after year.

The ease and certainty with which electric heating units can be controlled automatically must also be given its full share of credit. The human factor with all of its inherent tendency toward forgetfulness and toward variation from time to time is absolutely eliminated by this method.

Since the introduction of continuous electrical methods it has been possible to make semi-scientific investigations in the industrial field, and several notable pieces of work have been done

FIG. 1.

along these lines. As a result of one such investigation, the japanning in one large plant has been reduced to what is practically an absolute basis. In this case practically everything is controlled automatically and one individual located in front of an instrument board some distance from the ovens and out of sight of all operations has general supervision of the entire process and is responsible for results.

Certain interesting facts have been brought out in connection with the electrification of this art. It does not seem advisable to burden this paper with a discussion of all of them, and attention

will therefore be confined to one set of facts which is particularly illuminating.

At the time when electrification started it was customary to bake japan in direct-fired gas ovens, in most plants. In these ovens gas is burned within the space in which the work is enclosed, and the products of combustion bake the work during the entire process. Temperatures of the order of 180° C. (356° F.) were considered the maximum allowable, and from 1½ to 3 hours were required per bake. For good work, which was to show a fine finish and was to resist wear and weather, three or more coats were deemed necessary. It was found to be particularly difficult to be sure of obtaining a high gloss, and the weathering qualities of work made under what were supposed to be exactly similar conditions were remarkably diverse.

After many abortive efforts to find means of studying what actually occurred during baking it was decided to resort to the microscope, in the hope that surface structure might throw some light on the matter. The results obtained greatly exceeded anticipations.

A typical structure resulting from baking japan slowly in a direct-fired gas oven is shown in Fig. 1. This is a reproduction of a microphotograph. The straight and curved lines have no significance, the pock-marked surface being the feature of interest. Several perfect craters, which show at different points in the figure, indicate the probable origin of the pock marks as collapsed craters.

The formation of these craters seems to be typical of all baking methods in which the heating is done by means of hot gases bathing the work. It is possible that their occurrence may be explained by what may be called subsurface vaporization. Imagine, for instance, that the diagonally hatched part of Fig. 2 represents a part section of a piece of metal and that the horizontally hatched part represents a section through a coat of japan applied to the surface of the metal. Assume now that hot gases, such as heated air or hot products of combustion, pass horizontally over the surface as indicated by the arrows.

It is obvious that vaporization of the solvent will occur at the surface of the liquid japan and that the temperature of the surface will be raised rapidly. Chemical change will therefore occur

first at the exposed surface, and it seems probable that this surface films over rapidly. The condition would then be similar to that in a can of paint which has been left open to the atmosphere for several days; there would be a rather tough film on the side next the air with practically unchanged material below. If a can of paint in this condition be imagined to be heated from below to such an extent as to cause vaporization of some of the constituents one of two things must happen: either the vapor must work its way along the under side of the film until it reaches the wall of the can and escapes, or it must blow a crater in the film and escape in that way. In the case of japanned surfaces heated from the outside such subsurface vaporization could only escape through the surface, as there is ordinarily no break such as occurs at the wall of the can assumed above. The microphoto-

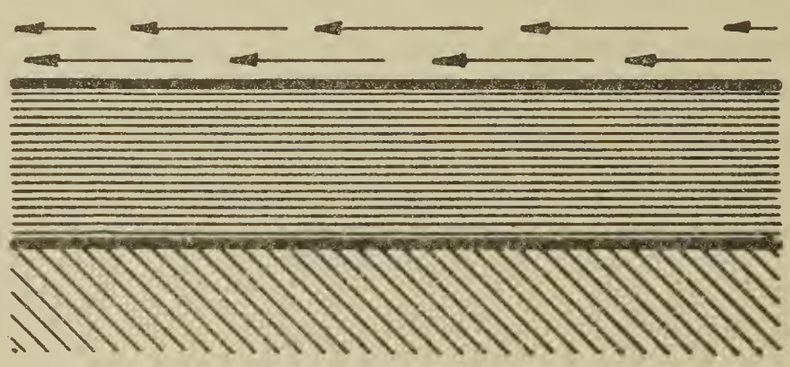

FIG. 2.

graph reproduced in Fig. 1 would seem to indicate that vapors do escape through the surface while this is still in a somewhat plastic condition.

These craters are probably partly self-healing as the process is ordinarily conducted, but it is obvious from the illustration that the healing is not perfect. A collection of such craters is all that is necessary to account for poor gloss and poor weathering qualities.

It would be expected that the crater formation would be least severe with very long bakes with gradually rising temperature, that it would be most severe with short time bakes and steep temperature gradients, and that a very short bake might actually result in pushing off flakes of the crater surface. No evidence of such flaking has been found, but finished work has been known to flake in a way which suggested the possibility of such a cause.

In Fig. 3 is shown a microphotograph of a piece of work directly comparable with that shown in Fig. 1. The metal was exactly the same in both cases, the pieces were prepared and dipped in the same japan, at the same time by the same man. They were dipped exactly alike and then baked, one in a direct-fired gas oven for 90 minutes and the other in an electrically heated oven for 45 minutes. It is obvious that the electrically baked piece has smaller and more evenly distributed craters, and that the surface is more perfect.

FIG. 3.

Similar comparative photographs of second and third coats show far more perfect surfaces resulting from electric heating. Reproductions of microphotographs of the third coats are given as Figs. 4 and 5. It is perfectly obvious that the electrically baked coat shown in Fig. 5 is much smoother and more perfect than the other which was baked by pure convection heating. It should be noted that many, if not all, of the large black spots which show in these two figures are small particles of carbon and that they were probably thrown out of the volatiles by a species of cracking, in contact with the air used for ventilation.

It is interesting to note that the baking of the coats in the gas oven consumed a total of five and a half hours while the three corresponding coats were baked electrically in two hours and forty minutes.

Inspection of pieces baked in direct-fired gas ovens and similar pieces baked in electrically heated ovens practically always shows that the electrically baked material has a higher and more perfect gloss or finish.

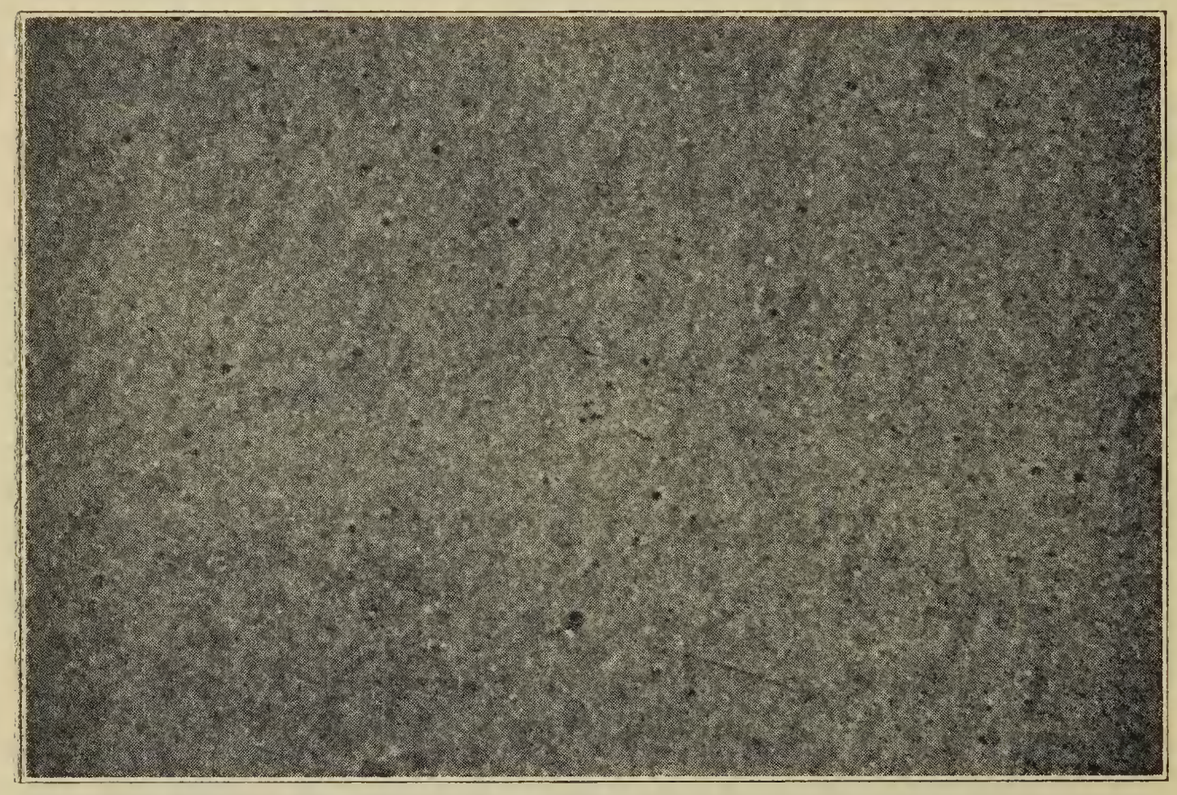

FIG. 4.

This could be accounted for by assuming some action between products of combustion and the japan itself, and some evidence seems to indicate such action under certain conditions. However, in view of the microphotographs already referred to and the explanation given to account for the craters, it seems more likely that the difference is due to the way in which heat is applied.

As a matter of fact, practically all heat transferred to the work in a direct-fired gas oven is carried to it by hot gases, that is the transfer is by convection. In an electrically heated oven at least part of the heat is brought to the work in the same way because of the circulation of the oven atmosphere set up by the presence of

the heaters. The rest of the heat is transferred by radiation from the hot heaters, and it seems probable that the action of the heat received in this way is different from that received by convection. It is at least probable that radiant energy penetrates the japan coat to a considerable depth before being entirely absorbed and converted into heat, and this causes more rapid setting of the inner portions of that coat.

If the craters are due to the causes assumed above, it should be possible to eliminate them entirely by baking the japan in a

FIG. 5.

reversed direction, that is, from the inside out. This can be done electrically by heating the metal itself either by the direct passage of current or by induced eddy currents.

Certain experiments were conducted on a small scale for the purpose of determining the relative effects of baking by pure convection, baking by combined radiation and convection and baking by heating of the metal itself. For this purpose similar samples, dipped in the same japan, were baked in bottles. For convection baking filtered air was heated to the proper temperature in an electric oven and was then drawn through a bottle in such a way

as to make it bathe the enclosed sample. For combined convection and radiation, the sample was surrounded by electric heaters enclosed with it in a bottle, the volatiles being drawn off and circulation being maintained by means of a small laboratory pump. For baking by internal heating the bottle and its inclosed sample were suspended in an alternating magnetic field of sufficient intensity to give the desired temperature gradient. Volatiles were removed during baking by a small laboratory pump as before.

Inspection showed the sample baked by convection heating to have the poorest surface and that baked by internal heating very obviously had the highest gloss and most perfect surface. It was hoped that reproductions of microphotographs of these samples could be given in this paper, but it was unfortunately impossible to prepare them in time for inclusion.

It is of particular interest to note that baking by internal heating is essentially an electrical method, and that it is far removed in every way from methods previously in use. It is further important to note that with this method a maximum metal temperature of the order of 170° C. (338° F.) and a bake of 15 minutes are perfectly capable of giving better results than can be obtained with external electric heating with 45-minute bake and a maximum temperature of 230° C. (446° F.). It also seems probable that one coat baked in this way will prove the equal of two or three baked by the older methods. The effect of all this upon energy charges for a given weight of metal baked is perfectly obvious.

It seems hardly necessary to discuss at greater length the various phases of the japanning art. It should be evident that electric heating opens up opportunities for improving the product and the production methods used in obtaining that product. It should also be evident that electric heating is capable of reducing factory operations in this field to so exact a procedure that accurate laboratory control is made possible. With industrial conditions brought to this point it becomes possible for research chemists to work to advantage toward the improvement of the japans themselves and toward the improvement of the methods of their utilization.

An equally promising field exists in foundry core rooms. The baking of foundry cores is at present a most haphazard process in the majority of foundries. A casual inspection of one batch of exactly similar cores will generally show colors varying from a light tan, or even lemon yellow, to a dark chocolate brown. One of the numerous varieties is certainly better than all the rest, and it would seem desirable to determine which one is the best for a given set of conditions and then to make all of them like it.

Preliminary experiments conducted for the purpose of discovering whether the essential properties of cores varied as greatly as their colors gave most astounding results. Strength was taken as reference in this case, although admittedly it is only one of numerous properties which must be considered in defining a perfect core.

One set of experiments was made upon exactly similar cores, made of the same materials and tamped to the same extent. They were baked at different rates and also with different maximum temperatures. Curves of strength plotted against time of bake and also plotted against maximum temperatures were sharply domed in all cases, and showed variations of several hundred percent in any one case. Samples of these cores were shown to experienced foundry men after rupture so that both exterior and interior were visible, and they picked out, as good, cores which had shown relative variations of over 100 percent.

Another set of experiments were made to determine the effect of air circulation. Again a number of exactly similar cores were tested. Baking methods were alike in every respect excepting for the quantity of air drawn over the core during baking. Strength of core was plotted against quantity of air passed in unit time, and again a sharply domed curve was obtained. Apparently, excess air is detrimental, though not to the same extent as a deficiency of air. What is most important is the demonstration that some definite quantity of air gives the best results.

It seems probable that investigation will show that porosity, brittleness, character of surface, and all of the other properties which must be considered in connection with cores will be affected in some such way as strength has been shown to be affected by the variables studied. If this is true, it certainly seems as though

the foundries which carefully study their production methods and costs will ultimately demand more perfect control of the core-baking process. When this time arrives it seems probable that electric heating will play a part similar to that which it has played in the japanning field during the past few years.

As a matter of fact, there are now in operation several electrically heated core-baking ovens, and their users all appear highly enthusiastic over the results attained.

The core problem appears to the author as one of the most promising fields for combined chemical and engineering investigation, and he feels certain that improvements such as those shown possible in japanning will appear insignificant in comparison with those which are possible of attainment in the core room.

Japanning and core baking have been used as examples because of the tremendous extent of both of these industries, and because it happens to be possible to record the results of a small amount of experimental work in both of these fields. It must not be assumed, however, that they represent the only possibilities for the application of electricity to low-temperature baking.

There are numerous other low-temperature baking processes, and the majority are in the same undeveloped state as are the two cited above. One very important field in which little has been done is the baking of foodstuffs, such as bread and other cereal products. Electric heating has been applied to the baking of such materials in several cases with very gratifying results, improving both the appearance and quality of the product.

In conclusion, it is well to call attention to the fact that the introduction of electrical methods for such purposes as enumerated above should be of particular interest to the chemist, because it makes it possible to reproduce on an industrial scale a sequence of operations and conditions which have been worked out on a small scale in the laboratory. It makes it possible to control industrial production to the same extent that laboratory investigations are controllable, and it thus opens to the chemist in the industrial field a tremendous opportunity for improvement of product and increased production.

DISCUSSION.

F. A. LIDBURY[1]: I consider this to be one of the most useful papers the Society has had presented to it for a long while. Some members may have had doubts as to whether this kind of subject was electrochemical in its nature, but I do not think one need waste very much gray matter on academic questions of that kind in view of its tremendous importance, an importance that is not merely a future one, but a present one.

Now, in calling attention to the conditions which govern the possibility of the application of electric heating to low-temperature reactions, the author wisely stressed the fact that you cannot show in most cases a direct saving in energy cost. But from the point of view of commercial efficiency you must take your whole cost sheet, and the author has called attention to a number of factors which outweigh any increase in energy cost in direct heating. In many cases, as he has pointed out, the speeding up of the operation brings with it not only other decreased costs, but even, in some cases, actual decrease of energy cost.

In certain well-defined instances of chemical reactions, above all those reactions in which the temperature limits must be held very closely, and in which a wide range, or even a comparatively narrow range, is not permissible, automatic controlability of the supply of energy is of vital importance. This happens to be particularly easy when you are employing electrical energy, not only because of the degree to which the control appliances are developed, but also because of the smaller mass and thermal capacity of the furnace setting.

With low temperature electrical heating every man has to be his own heating engineer. The science of electrical heating is in unsatisfactory shape, because of the fact that it has never been properly studied. Even in a number of plants which manufacture electrical heating appliances, the engineering data which ought to exist is lacking. Much work must be done on this subject, and the results published.

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The problems, however, are not very difficult. Electric heating has been chiefly applied in places where the problems are much more difficult than those which involve only the maintenance of these comparatively low temperatures. The materials which can be used for this kind of work are extremely varied, and they can, in a good many cases, be obtained extremely cheap.

Intensity of heat output per unit area of the heater should be avoided in low-temperature apparatus because it causes quick deterioration of the heating element, and is inconsistent with a uniform distribution of heat over the whole surface.

CARL HERING[2]: It seems to me that in these drying and baking operations too little thought is given to the degree of saturation of the surrounding air or gases. If very dry, in the sense that they contain very little vapor of the solvent, there will undoubtedly always be formed that crust or skin on the outside which checks the drying out of what is below it. This skin may afterwards crack or be punctured by the vapors from the wet material below it. The degree of saturation of the surrounding gases was touched upon in the paper, I believe, in connection with core drying.

The author suggested heating the coated metal electrically by passing a current through it. That is very nice in the theory, but if some one was to ask me, as an electrical engineer, to arrange a system for passing an electrical current through such an object of such complicated form as an automobile body, to heat it to a uniform temperature, I think I should say that I was too busy. But there are more practical ways of doing it electrically, such as by hysteresis, though I think that would develop hot spots. It seems to me that the most promising way is by means of Foucault currents, allowing time for the localized heat to distribute itself.

W. S. SCOTT[3] (*Communicated*): This paper mentions a list of variable factors, the controlling of which is made possible by the use of electric heaters and suitable control equipment. Since the application of electricity to japanning or enameling constitutes one of the latest developments in the industrial heating field, it may not be inappropriate at this time to discuss briefly the

[2] Consulting Electrical Engineer, Philadelphia.
[3] Commercial Engineer, Westinghouse Elec. & Mfg. Co., East Pittsburgh.

electrical equipment required and the forms of control for meeting existing operating conditions, which are becoming more and more exacting.

The heating unit consists of a ribbon-type heater, rated at 2.5 kw. at 120 volts. Any number of these heaters may be installed in an oven, and connected to any power circuit which may be normally supplied—direct current, single-phase or poly-phase alternating, 110, 220 or 440 volts.

Where it is desirable to control the oven from a distant point, magnet switches are used. This method of operation is employed in large installations where one man is placed in charge of the operation of all the ovens, and is held responsible for the maintenance of the proper temperature at all times. Thermo-couples are used for indicating the temperatures in such cases, the wires from all the ovens being brought to a control desk at which the man who has charge of the operation of the ovens is located.

In most installations it is desirable, and in fact, one might say essential, that the temperature of the oven be held constant, continuously and entirely automatically throughout the working day. The accomplishment of this feature necessitates the use of a thermostat, with suitable relays, to be used in connection with the magnet switches.

It is rapidly becoming the practice to install individual exhaust fans in connection with each oven, for the purpose of insuring proper ventilating conditions. When natural ventilation afforded by the use of a high stack is depended upon, the ventilation is not a constant quantity, but varies from day to day, depending upon humidity, air temperature, and wind. Even with an exhauster, the ventilation will become impaired in course of time by the heavy oily vapors condensing in the vent pipes, forming a tarry substance which finally solidifies and cakes. Thus the vent pipes gradually become restricted in useful cross sectional area, with the possibility that in course of time the ventilation will become so impaired as to prevent the escape of the volatile naphtha vapors before an explosive mixture is formed. This condition may be overcome by using a motor-operated exhauster. In the first place, the power for operating the main magnet switch is taken from the exhauster motor circuit, and connected back of the starting switch, thereby eliminating the possibility of the

oven being operated without the exhauster. In the second place, it is known that the power required to operate an exhauster or blower varies with the amount of air passing through it. While in this case the power would not vary directly with the amount of air handled, the variation is sufficient to enable an instrument to be calibrated in such a manner as to give a close indication, by the decrease in current input to the motor, of the degree to which the vent pipe has become stopped up. Further, if a relay be inserted in the motor circuit, with a suitable coil and short-circuiting plunger, the stopping up of the vent pipe, whether caused by the vapor condensing in the pipe, accidental closing of the damper, or a piece of work falling off the conveyor across the vent opening, will be followed by a decreased input to the motor, decreasing the current flowing in the current coil to such an extent that the magnet no longer has sufficient power to hold up the plunger and weight, allowing it to drop, short-circuiting the two auxiliary contacts, which in turn short-circuit the thermostat relay-coil, causing the main magnet switch to open. Thus with a properly-equipped electric oven, the danger from explosions of volatilized oils may be entirely removed.

H. M. LANE[4]: Something has been said about cores and core binders. It has been my business for a good many years to make researches along that line. The problem varies between the extraction of four percent of water to dry down your compounds, in the case of steel foundry moulds, up to cases where you must take out over ten percent of water, and then perform a chemical reaction.

I have experimented with several hundred core binders, with drying oils, gums, waxes, paste, tars, pitches, etc. If it is japanning, it is simply part of a baking proposition. If it is an oil-stained core, of the linseed type, it is a paint or drying proposition. If it is a steel-foundry mould, it is practically a pottery proposition.

Some years ago I had in a steel foundry two batteries of core ovens side by side drying the same product, and one battery was fired with coke and one with natural gas. I could not imagine why in time I got better results out of the coke-fired drying oven until I realized that a large part of the products of com-

[4] Industrial Engineer, Detroit, Mich.

bustion of the natural gas was water, passed through the oven as superheated steam, and did practically no real drying work. Putting on a forced draft system, I found I got good drying down at the bottom, but I also found a radical difference in temperature in different parts of the oven, some 350° to 400° F. (200 to 225° C.) between the hottest and coldest part of the oven, and the problem was to produce a uniform temperature. If you try to do that electrically, you meet downward currents of the moisture being extracted. I experienced that in drying pottery. As the moisture is extracted from the upper cores or molds by the heating element, it flows downward, and provision must be made for heating the bottom of the oven. I do not believe that any electrical core-drying oven will be a success without a proper consideration of the mechanical circulation.

H. K. RICHARDSON[5]: There has been an inquiry for a japan that has no volatile solvent. That inquiry was answered a thousand odd years ago. Native Chinese lacquer has no volatile solvent. It is put on by an ordinary native on a day when the weather is damp and mucky. He would not put it on on a day when the sun is shining. It dries on a wet day and does not dry on a clear dry day. The reason of that I do not know. I have often watched the natives put on lacquer and always found that if the lacquer is put on on a day when the sun is shining and the temperature is high, a tacky, rough surface results that catches up the dust, and it will take somewhere between four and ten days to dry, and never be satisfactory; whereas if one waits for a day when the humidity is high, a real nice mucky day, you can put the lacquer on at about six o'clock at night, and by three or four o'clock the next morning you have a beautiful, hard, dry, clear surface, just like all this high-grade Chinese lacquer you see. Whether it is a hydration process that goes on, or whether the process is one of oxidation, I cannot say. All the lacquer contains is the native lacquer or the tree sap thinned down with pure China wood oil in which there is no volatile solvent.

C. P. MADSEN[6]: I can hardly let the arraignment by Mr. Lidbury, of the heating art in general, go unchallenged. It is true that there does exist a very "unsatisfactory situation" commer-

[5] Research Laboratory, Scovill Mfg. Co., Waterbury, Conn.
[6] Electric Heating Engineer, Newark, N. J.

cially in the electric heating art, but extending that criticism to the engineers and designers is hardly warranted. It is also a fact, unfortunately, that many companies which manufacture electric heating devices have no engineers.

It is unreasonable to presume that a company whose obvious business is that of making domestic heating devices, intended to be used in lamp sockets, is necessarily in a position to furnish properly designed devices for industrial purposes. There are at least three such companies who have an industrial department, and who will either furnish a man that which he wants when he knows what he wants, or will tell him what he wants if he does not know it.

It is possible to get resistance materials for resistors which are quite durable and will answer the requirements for this class of work, without using any materials which are patented or upon which it is necessary to pay royalties.

In japanning electrically, one must consider that it is only partly a vapor process, but mainly a chemical one. I am told by paint engineers that the solvent should be removed from the japan before the temperature is raised, and that the principal phenomenon is not the evaporation of the solvent, but the oxidation of the linseed oil, which good japan should contain, and a high temperature is required for that purpose. The drying characteristics of the native Chinese lacquers are due, I think, altogether to the China wood oil, which they use instead of the linseed oil. I am told that this is the principal secret of the oriental lacquers, and that the reason they behave differently while drying is that this oil has the property of polymerizing and solidifying throughout its whole depth, rather than by drying from the surface inward.

F. A. LIDBURY: The electric heating art is not in satisfactory shape, because it has not a literature that is commensurate with its importance, or even with the amount of work that has been put into it.

C. F. HIRSHFELD: Mr. Lidbury called attention to the fact that energy cost is not necessarily the vital point in many of the processes which are of the type referred to in this paper.

Taking japanning as an example, practically all of it was done by means of coal or coke firing up to ten or fifteen years ago.

Within the past few years practically all japan users in regions where gas was available adopted gas, although it cost more per unit of energy. In this territory, for instance, the ratio of costs is of the order of 18 to 1 in favor of solid fuel. Why have they changed? Simply because the energy cost was so minor a part of the whole cost of the process that the control, the flexibility, that they secured more than warranted the increased expenditure. If a jump of that sort can be made, there is no reason why we should not take the jump from gas to electricity. The ratio of costs in this case is sure to be much smaller than the 18 to 1 I have just mentioned, and many times smaller when electricity is available at the low rates now prevalent in manufacturing communities.

Conditions are further modified by another feature. When you instal an electric heating equipment, you instal something which will continue to operate under exactly the same conditions day after day if the proper voltage is maintained. When you instal any kind of combustion apparatus using solid, liquid, or gaseous fuel, you are dependent upon the supervision of the operator or upon the functioning of more or less imperfect apparatus for the maintenance of efficiency and uniform conditions. In the case of gas burners, for instance, it is not at all difficult to so operate a gas burner as to get half the thermal efficiency from the gas used.

The ability to secure and maintain thermal efficiency is just as important as the ability to obtain energy at a very small cost. The energy cost itself, in many cases, is entirely insignificant, all things being considered, in comparison with the total cost of the process. You can very often forget entirely the cost of energy, and consider only the other features of the process.

In regard to the position of the manufacturers, the electric heating art, to be sure, is old, but the phase of it which we are stressing at this particular time is comparatively new. The greater part of it has been developed within the past three years. Every one was skeptical at the start; very few of us could then see beyond the energy cost. The manufacturers, justly, did not want to put thousands of dollars into the development until they were certain they were going to get at least some sort of return. Speaking perfectly frankly, the manufacturers, in so far as I have been able to observe, have co-operated most splendidly, and the larger

manufacturers have formed industrial electric heating departments and are spending comparatively large sums of money in experimenting and in developing. You cannot develop things of this sort over-night. The apparatus which is now being built, such as japanning equipment, is entirely different from what was designed two or three years ago.

In this connection I want to refer to a remark made by Mr. Madsen, possibly amplifying it a little bit. He called attention to the fact that in this low-temperature work it is not necessary to use some of the more expensive patented alloys in the heating units. The material of which the heating unit is made really depends upon two things: One is the fact that each heating problem carries with it what may be called a limiting temperature gradient and the other has to do solely with commercial considerations. Considering first the limiting temperature gradient, the heating unit may be operated at a certain number of degrees, possibly hundreds of degrees above the processing temperature. If, for instance, you operate with an oven at 450° F. (232° C.) the maximum permissible heater temperature may be 550° F. (287° C.) or some other similarly low value. In such a case expensive alloys are not required, and, normally, it would be foolish to use them. On the other hand, if the process permits the use of heaters operating at 1,800° or 1,900° F. (982-1,037° C.) in a 450° F. (232° C.) oven, then you have to use a more expensive kind of material.

From the commercial side, high-temperature units must be made of expensive materials, but only small surface is needed to dissipate a given amount of power in comparison with the greater quantity of cheaper material which may be used if the unit operates at a low temperature.

Within the limits set by maximum allowable temperature there is thus some best material, and that best material is determined by the commercial balance resulting from cost of material and allowable temperature gradient.

Mr. Madsen called attention to the fact that the user can make his own units in cases where the operating temperature is sufficiently low to permit the use of ordinary resistance materials. A word of caution seems desirable at this point. During the past three years we have had numerous opportunities to observe the

performance of units operating at comparatively low temperatures, and we have discovered that satisfactory operation and life depend upon numerous things which the amateur designer would very probably overlook in making his first units. Insulating materials which would seem to have satisfactory properties break down fairly rapidly under the complicated conditions characteristic of this sort of service. Joints which would be perfectly satisfactory under most conditions develop an astounding number of weaknesses. This list might be amplified to cover a half-dozen items, or more.

The manufacturer of heating devices has ample opportunity to note all such failures and to devise materials and designs which will be least apt to cause trouble, and it is my personal opinion that, in most cases, it is cheaper in the long run to purchase from such a manufacturer if he can supply apparatus suited to one's specific needs.

Dr. Hering yesterday spoke of the degree of saturation of the furnace atmosphere with respect to the vapors of the volatile materials. His statement is perfectly correct, but I think that it also will stand a little amplification. It is true that the physical state of the drying material, or drying film, or whatever it may be, differs with the saturation of the surrounding atmosphere with respect to the vapor of the material which is driven out during drying, but there are also a number of limiting factors, in some cases, which restrict your choice of the percentage of saturation permissible. For instance, referring again to japanning, the solvents, or diluents, which are now used, all form combustible mixtures with air. One of the arguments in favor of electric heating in this particular art is the fact that it may be made fireproof. If you are attempting to make a thing fireproof the best procedure is to remove every possible recognized hazard, and a combustible mixture existing within an oven is certainly a recognizable hazard. If, however, you supply sufficient air to dilute that mixture to a point below that at which it can propagate flame through its mass, you have practically removed that hazard. In this particular case, we have adopted this method, so that we are limited to a very, very low percentage of volatile vapor in the oven atmosphere, possibly too low for the best surface, although I am not ready to say that.

With regard to the question which Dr. Hering raised as to how we would heat an automobile body internally, I confess I do not know, but it may interest you to hear some of the things which we have done, at least experimentally. The most obvious method of heating internally is to pass a current through the object being heated, and I call your attention to the fact that a windshield frame, for instance, can be treated very easily in that way. Again, a cylinder open at both ends may be heated by making it a short-circuited secondary. With pieces of more complicated shape, we have obtained satisfactory results by using hysteresis and eddy currents.

I have simply mentioned this phase of the subject to show the direction in which we are going, and if this internal heating proves to have the advantages which it seems to have at first sight, I feel perfectly certain that each problem will be treated as a special proposition and that the necessary methods will be devised. I confess perfectly frankly that I do not see how to apply this method to, let us say, an automobile mudguard, or to a complete automobile body. That does not mean that it cannot be done. If we find the way to do it with the simpler thing, we may find the way to do it with the more complicated.

Mr. Lane made some remarks with regard to the necessity of obtaining an absolutely uniform temperature distribution throughout a core-oven. That is true so long as you confine the consideration to what we may call the box or kiln type of oven, where the oven is of such size and shape that convection currents are bound to result from an uneven temperature distribution, unless you prevent them by the actual formation and control of countercurrents. However, there is another solution, and that is not to use, or to try to use, a uniformly distributed temperature. For instance, the proper way to bake a certain type of core is not to put it in an oven at a certain temperature and keep it at that temperature a certain length of time, and then remove it. The proper way is to raise its temperature from that of the room to its baking temperature along a certain temperature gradient which brings it to the maximum temperature in a certain length of time, to hold it at that temperature the necessary time, and then to cool it along a certain temperature gradient until it is brought back to the room temperature. That might be done by putting the core

in a box and bringing the box temperatures successively to certain values, or it might be done by passing the core through a long tunnel of definite cross section, with definite temperature zones, with the piece passing successively from one zone to the next. This is really the most promising and the simplest method of carrying out the process, when it can be done. It is particularly applicable to modern production methods where you have numerous similar parts, all to be dried in exactly the same way.

While it may sound peculiar, the answer to Mr. Lane's question, under modern large production methods, is to get the result of a perfectly distributed, uniform temperature by using exactly the opposite, a properly graded temperature variation.

Concerning the use of extremely high steam pressures and temperatures, you will find a piece of apparatus described by Robert Cramer, in the Transactions of the American Society of Mechanical Engineers, January, 1916, in which he gave a description of a boiler which is to be built for commercial use in large sizes for pressures up to about 600 pounds per square inch and in small sizes up to about 1,500 pounds. The boiler is made of small steel tubes, all welded together.

W. C. Brooks[7]: As you all know, one of the greatest faults with the present methods of japanning is, as Mr. Hirshfeld mentions, the fire hazard. We made an attempt to solve the problem, and called into consultation a manufacturer of enamels and also of electrical heating apparatus; we attempted to get out a japanning oven which would be perfectly safe. But the electric heating company immediately replied that we could not use electric heating units in this oven at such a low temperature as would not ignite the gas, and they went no further with the matter on that account. So we considered another method which accomplished the purpose suggested by another gentleman here, and that is of getting the proper amount of saturation of the atmosphere to prevent a skin forming on the japan. That was accomplished by simple radiant heat. We made the oven in two compartments, an outer compartment, of annular chambers, heated by either gas or electricity, and the inner compartment, with an entirely separate ventilating system, which we could control to

[7] Chemical Engineer, National Carbon Co., Cleveland.

our satisfaction, and thereby get the kind of atmosphere we wanted. The furnace was merely a thin steel shell of about 22 gauge sheet-iron, heated by radiation; in fact, similar to a baker's oven. That has given us the atmosphere we want, and at the same time we can use either gas or electric heating with comparative safety.

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 5, 1917, President FitzGerald in the Chair.

A SWITCHBOARD FOR EXPERIMENTAL ELECTRIC FURNACE WORK.

By W. L. Badger.

[*Abstract.*]

Description of a cheaply-constructed switchboard for laboratory use, especially arranged to give great flexibility of current when operating small electric furnaces.

In deciding on equipment for laboratory work with electric furnaces, the author found little or nothing in the existing literature except brief mentions of very elaborate arrangements. The only thing which approached his requirements was an arrangement described by FitzGerald (Trans. Am. Electrochem. Soc., **26**, 229). This did not offer quite the capacity he desired without a cost as high as the present set-up, and at the same time did not give great enough flexibility. The present description is offered in the hope that it may be of service to others in similar circumstances. It should be made plain that the author does not claim credit for the ideas involved, but only for the details of the arrangement. The board is built around ideas embodied in one constructed by Dr. F. C. Frary for the University of Minnesota in 1908; and the transformer is a duplicate of the one he used.

The conditions which the equipment was to fulfil were that it should give wide variations in voltage by as small steps as possible but at as nearly full rating as possible; that connections should be made quickly and simply; that it should be foolproof; and that the cost should approximate $300. It is believed that these conditions are more nearly met than by any of the arrangements suggested by the companies who were invited to bid on the proposition.

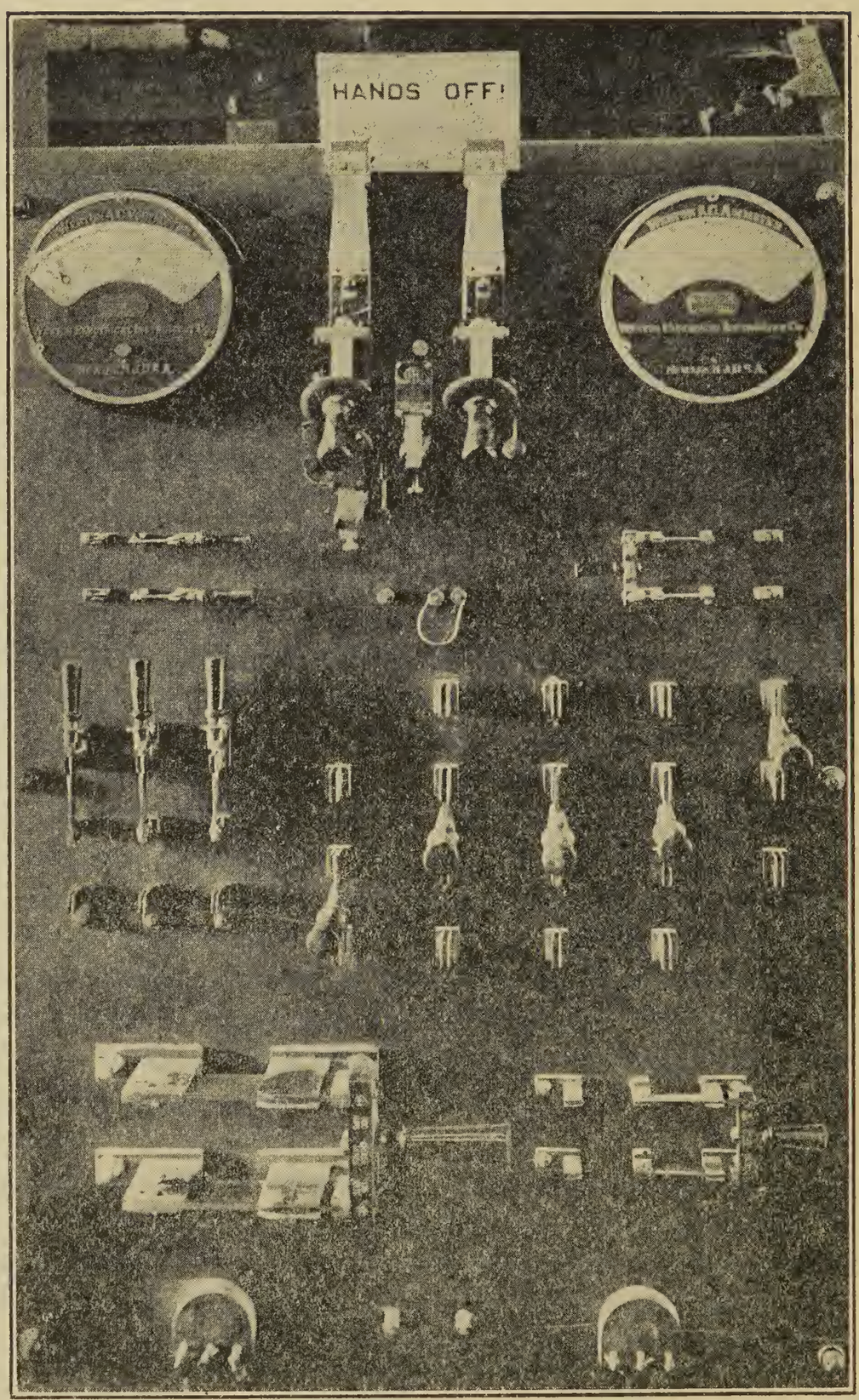


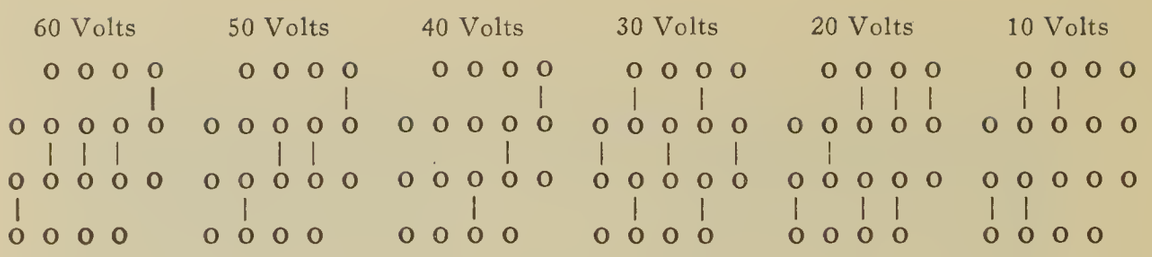
FIG. 1.

The transformer is rated at 10 K. V. A. and is built for 230 volts on the high-tension side. The high-tension winding has five taps, so that low-tension voltages of 10 percent above nominal, 5 percent above nominal, nominal, 5 percent below, and 10 percent below, may be obtained. On the low-tension side are two 10-volt coils and two 20-volt coils. The transformer was obtained from the Enterprise Electric Co., Warren, Ohio.

The board is shown in Fig. 1, and a diagrammatic sketch of the wiring in Fig. 2. The supply line is connected to a double-pole circuit breaker shown at the top of the board. This is provided with both overload and shunt release coils. From the breaker the current passes to the double-pole double-throw switch *I*, which connects the 220 volts either to the bus-bars direct, or to the high-tension side of the transformer through the three single-pole double-throw switches *E*, *F*, and *G*. The five taps of the high-tension winding are connected to these as shown by the numerals. The connections are as follows:

Switches			Voltages generated in low-tension coils
E	*F*	*G*	
down	down	down	10 percent above nominal
down	up	down	5 percent above nominal
up	———	down	nominal
down	up	up	5 percent below nominal
up	———	up	10 percent below nominal

The connections of the low-tension coils are made by means of the four rows of knife-blade fuse-clips shown at the right side of the board. The four upper clips are connected by a bus-bar, as are also the four lower ones. The low-tension coils are connected diagonally across the two middle rows as indicated. The extreme left clip of the second row and the extreme right clip of the third row are to form a bridge in making the 30-volt connection. Connections are made by short copper bars with suitable handles, which can be plugged into any pair of clips in a vertical line. By this means any combination of series, parallel, or series-parallel connections can be made; giving low-tension voltages of 60, 50, 40, 30, 20, or 10 volts at ratings of 100, 83, 67, 100, 100, and 33 percents, respectively. The connections are shown below:



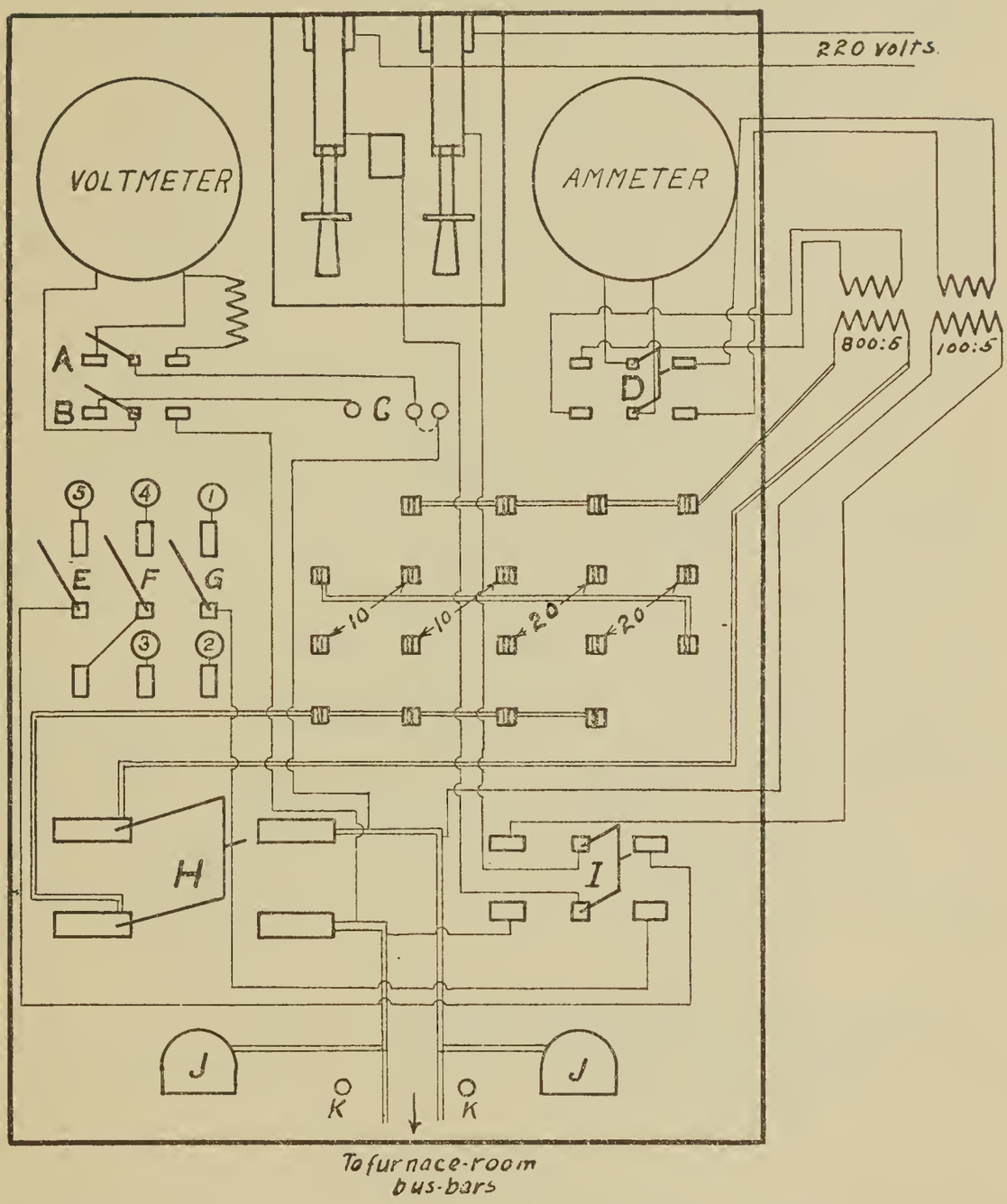
With any one of these arrangements the voltage may be varied through five smaller steps by means of the switches *E*, *F*, and *G*, as shown above. The result is a very flexible arrangement, particularly suitable for granular carbon resistance furnaces where there is a wide range of resistance, as temperature changes. The actual voltages delivered when no current is being used are as follows:

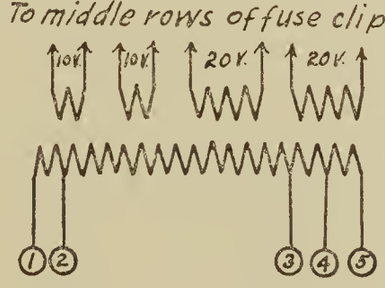
64.5	53.5	43.0	32.5	21.5	12.0
61.5	51.0	41.0	31.0	20.5	11.5
59.0	49.0	39.0	30.0	20.0	11.0
56.0	46.5	37.0	28.5	19.0	10.5
53.5	44.5	35.5	27.5	18.0	10.0

From the low-tension connections the current passes through the ammeter transformer and then to the furnace-room bus-bars. A pair of terminals (*J*) is added so that current may be taken directly from the board. The voltmeter is so connected that it can be used to read the voltage on the bus-bars or the voltage across the binding posts *C*. By this latter arrangement it is possible to take the voltage drop across any part of the furnace. At the bottom of the board is a pair of binding posts (*K*) to which the shunt coil of the circuit breaker is attached. By means of a 220-volt push-button the breakers may thus be tripped by the person working at the furnace.

Since the bus-bars may carry both 220 volts and the low-voltage current, both ammeter and voltmeter have double scales. The voltmeter reads 0 to 75 or 0 to 350 volts, the change being made by the switch *A*. The low-tension circuit includes an 800 to 5 transformer, and the high-tension circuit a 100 to 5 transformer.

The writer has a few suggestions to make if the board were to be duplicated. The ammeter transformers should be arranged so that either high or low scale could be used with either high- or low-voltage currents. The board as here shown is only 3 ft.





TRANSFORMER BOARD
FOR
ELECTRIC FURNACES.
Chemical Engineering Dept.
University of Michigan.

FIG. 2.

(90 cm.) wide, because it was built to fill a particular space, but a larger board would be desirable; especially as regards the connections on the rear of the board. If the main low-tension switch *H* is closed, the switch *I* cannot be thrown to the left; but if the switch *I* is thrown to the left first, it does not interfere with closing switch *H*. The result is to short-circuit the 220 volts across the low-tension coils of the transformer. This was foreseen, but the circuit-breakers were relied upon to protect the transformer in such a case. A board to be used by students, however, must consider such possibilities as holding down the breaker handles; so that an arrangement which would absolutely prevent the short-circuiting of the low-tension coils would be an improvement. Lastly is the possibility of producing dangerous voltages by opening switch *D* (controlling the ammeter transformers) while current is on. The only way the writer is able to feel safe about this is to give repeated personal warnings to every man who may have occasion to use the board.

This board has been in operation for two years, and the average student grasps the details without difficulty. It is better to provide him with a blue-print of the connections, in which case there is no trouble at all, even with students who have had only a little electrical engineering. The board was built in the University shops and cost (in 1915) a little over three hundred dollars.

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DISCUSSION.

GRANT C. MOYER[1]: To provide for cases where rapid change from one voltage to another is desired, it would be better to have the high-tension taps on the transformer numbered 0-1-2-3-4-5 and the switches marked *E, F, G*. The connections could then be pasted on a chart, as:

[1] FitzGerald Laboratories, Niagara Falls, N. Y.

0-3-3	10% above nominal.
0-4-2	5% " "
5-2	nominal.
0-4-1	5% below nominal.
5-1	10% " "

The connections of the low-tension coils, as made by the rows of knife-blade fuse clips, should also be numbered for quicker

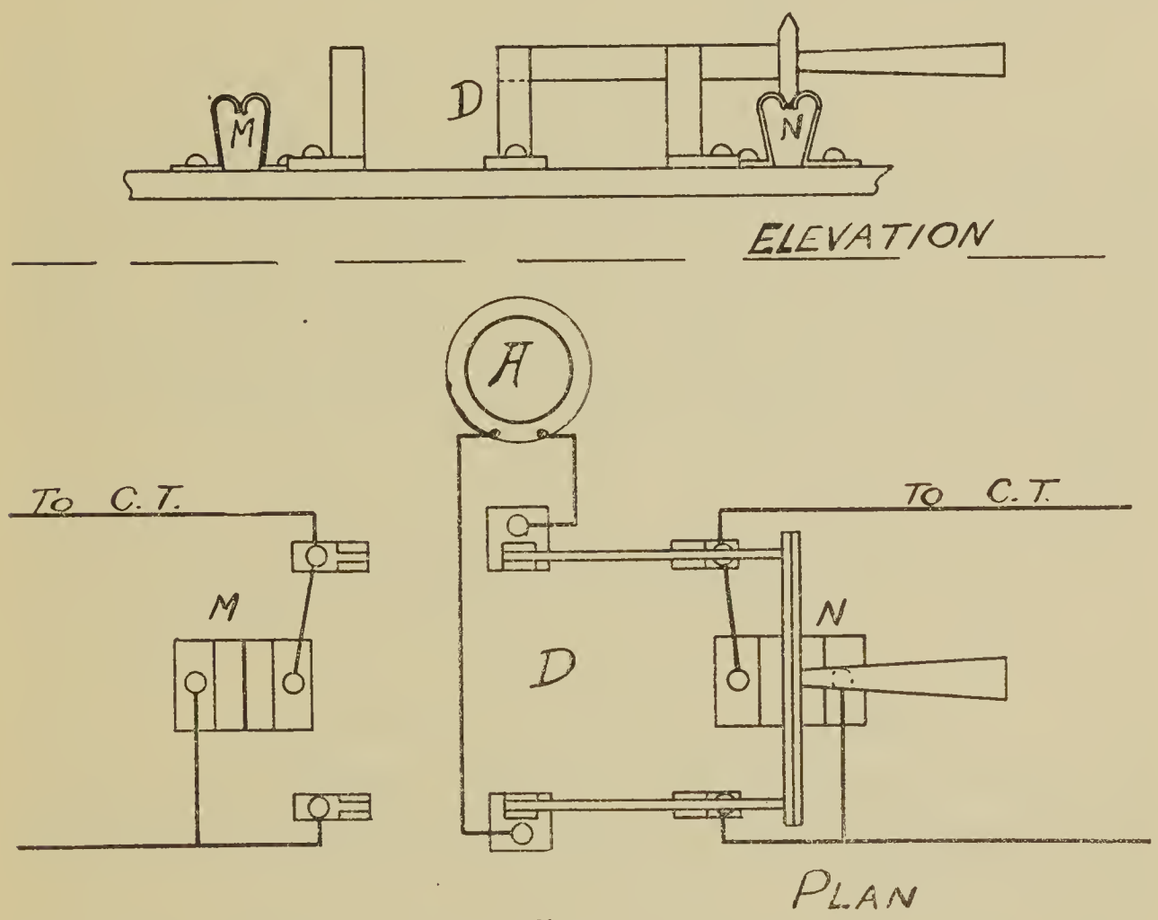

FIG. 3.

working. Thus, numbering these contacts from 6 to 18 consecutively, we would have in addition to the chart as shown in the paper, the following table:

60	Volts	9-11-12-13-15
50	"	9-12-13-16
40	"	9-13-17
30	"	6-7-10-12-16-18
20	"	7-8-9-11-15-17-18
10	"	6-7-15-16

On page 162 mention is made of the danger of short circuiting the 220 volts across the low coils of the transformer, and depending on the circuit breakers for protection. A very simple attachment to the handle of the switch *I* would prevent all danger. An extra handle or knob high enough that when switch *I* is thrown to the left it will act as a stop to prevent the switch *H* from being thrown in. A hole in the switchboard would allow the handle or knob to pass through it, when *I* is thrown over to the contacts on the right.

A simple device to prevent danger from opening switch *D* and burning out the ammeter transformers is shown in Fig. 3. *M* and *N* are spring contacts connected across the lines leading from the switch *D* to the current transformers. They are so placed that when the switch is closed the contacts are spread and allow the current to pass through the switch to the ammeter. If the switch is opened, the contacts spring together and short-circuit the transformers. By such arrangement as this the current transformers are always short-circuited when the ammeter is not in circuit.

W. L. BADGER: Mr. Moyer's remarks about numbering the connections would perhaps enable a student to learn the connections quicker. In actual use it is found that the connections cannot be made quickly if the student has to refer to a diagram or chart of any sort. A very little use, however, serves to fix in the student's mind the *looks* of the proper connections. In every case I have observed that the man soon remembers the appearance of the board and depends on this rather than a table or printed directions.

The device to prevent danger of throwing the 220 volts across the low-tension side of the transformer would be very satisfactory. If another board were to be built by the writer, he would omit entirely the provision of 220 volts on the bus-bars. There is an element of danger in having 220 volts available on circuits where during most of the time the voltages are so low that the user needs pay no attention to them. Properly built granular carbon furnaces seldom if ever need such high voltages to start them.

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 3, 1917, President FitzGerald in the Chair.

THE GRINDING WHEEL—A CONNECTING LINK BETWEEN THE ELECTRIC FURNACE AND THE AUTOMOBILE.

By Richard G. Williams.*

[*Abstract.*]

A discussion of the various artificial abrasives and their uses. Dividing into the aluminous group and the carbide of silicon group, there is discussed the raw material, electric-furnace manufacture, and the further treatment of the crude material to produce the abrasive in grain form. Following is a description of the manufacture of grinding wheels of different types, their composition, forming, heat treatment, vulcanizing, truing, testing, inspection, packing and shipping. The working characteristics of the wheels thus made, and particularly the use of various kinds and sizes in the manufacture of automobiles, is described.

MANUFACTURE OF ARTIFICIAL ABRASIVES.

The words "abrasive wheel" are perhaps more indicative to an electrochemist and "emery wheel" to some automobile manufacturer than the words "grinding wheel." However, the manufacturer of grinding wheels is of the opinion that neither "abrasive wheel," nor "emery wheel" really fits the situation, and so prefers the words "grinding wheel." Emery is only used to a very slight extent at present, and since an ordinary barnyard sandstone is an abrasive wheel, it is hardly correct to use abrasive wheel either, because the modern grinding wheel is an efficient cutting tool and must not be confused with sandstones and emery wheels.

The success of the modern grinding wheel is dependent to a very large degree upon a product of the electric furnace, namely artificial abrasives. Artificial abrasives are of two kinds, or two

* Mechanical Engineer, Special Investigator, The Norton Company, Worcester, Mass.

groups, the aluminous group and the carbide of silicon group. The first contains aluminum oxide as the main constituent, and the different materials vary quite widely in physical properties, according to their chemical composition and electric-furnace treatment; while the carbide of silicon abrasives, forming the second group, vary but slightly in chemical composition and physical properties. These groups of artificial abrasives vary in characteristics almost as much as the different alloy steels which have been developed in the electric furnace by the initiative and resource of electrochemists. No product of the electric furnace, however, has a larger field of importance, nor has more profoundly influenced modern mechanical production and methods than artificial abrasives. In view of the fact that the automobile industry is probably the best example we have of rapid production, and advanced modern methods, you can readily appreciate the importance of artificial abrasives in this industry, and a short description of the manufacture of abrasives will be in order.

Considering first the aluminous group, the raw material must necessarily be a substance high in aluminum oxide. The most satisfactory material is a high-grade bauxite, although satisfactory abrasives are being made from other materials, such as low-grade bauxite and emery. Aluminous abrasives are made in the arc type of furnace. These furnaces often consist of a wrought-iron shell, or some form of pot lined with carbon. The electrodes are suspended in the pot and then lowered to the bottom of the furnace, a train of graphite or fine coke placed between the electrodes, the current turned on and an arc suitable for fusing is available as soon as the train of graphite or coke has volatilized.

Before fusion in the electric furnace the bauxite receives a calcining treatment to drive off 30 percent of combined water. Suitable chemicals are mixed with the calcined ore in order to facilitate the removal of such materials as iron and silicon. Furnaces of three-ton capacity consume about 650 to 700 horsepower and it takes approximately 24 hours for a furnace run. After the run is completed the shell is stripped off or the furnace sides removed and the pigs allowed to cool. When the pigs have cooled to a sufficient temperature, they are broken up by sledge hammers into pieces convenient for putting through a large jaw crusher. This operation reduces the material to pieces about the size of a

man's fist, and in this condition the abrasive is sent to the grinding-wheel factory for further treatment.

The carbide of silicon abrasives have been described so many times that it hardly seems necessary to again mention their manufacture, particularly to the American Electrochemical Society. In order to have the subject complete, however, a few remarks will be given.

The resistance type of furnace is used. The heat radiated and conducted from a central core of finely ground coke is used for the formation of the abrasive. The raw materials are coke, sand, sawdust, and a little salt, the object being to extract the carbon from the coke, the silicon from the sand and tie these up in the ratio of 1 to 1. It takes about thirty-six hours for a furnace run and approximately 1,000 horsepower is consumed. After the furnace has cooled considerably the outside layer of semi-decomposed materials is stripped off, and carbide of silicon is found to exist in a comparatively thick shell around where the coke core originally existed. It is an easy matter to break this shell up into pieces convenient for handling. The material is then sent to the grinding-wheel factory.

PREPARATION OF THE ABRASIVE GRAIN.

When the crude abrasive in lumps ranging in size from those that will pass through a 6-inch (15 cm.) ring and smaller, are received at the grinding-wheel factory, the first step in the production of grain to be used in grinding wheels and other products such as oilstones, rubbing bricks, refractories, and so forth, is to pass through powerful crushers, equipped with manganese steel jaws. This operation reduces the material to small lumps. It is further reduced from lumps to grains by passing through succeeding rolls, each set being somewhat smaller than that preceding. In this way a range of sizes from very coarse to very fine is produced.

Some abrasives as received in the grinding-wheel factory contain an appreciable proportion of material which is magnetic and which is detrimental to the manufacture of wheels. This material is, therefore, removed by means of a magnetic separator.

The next step is washing. The material is placed in suitable machines and by means of agitating devices in connection with

a current of water, the very fine sizes and dirt or dust which the material may have picked up are thereby removed. After washing, the material is dried in a very simple type of dryer. This consists of boiler plate shell, on the inside of which are longitudinal vanes. The shell is tilted somewhat, revolves slowly and the material allowed to fall upon a series of steam coils which are located in a central position inside the shell.

The final operation is sizing. The material is fed in a uniform stream on top of horizontal screens which are mechanically agitated. The resulting average size of grain depends upon a number of factors, among which the following are mentioned: Amount of feed, speed of agitation, length of the strokes, size of the wire in the screen, and size of the aperture.

To produce very fine grains which are referred to as flours, hydraulic classifiers are used. The basic principle is the same as in any type of hydraulic classification, namely the material to be sized is introduced into water moving with a definite velocity. The velocity is sufficient to carry away the finer portion of the material, while the rest is heavy enough to remain in the original container. It might add interest to describe various pieces of apparatus, but as each piece is special and the product of careful experimentation, it would not be in order to go into detail in a general paper of this type.

MANUFACTURE OF GRINDING WHEELS.

The term "grinding wheel" as here used is intended to apply to wheels made by bonding abrasive in a suitable manner and then subjecting the whole to heat treatment. This distinguishes a grinding wheel from a grindstone, which is nothing more or less than a piece of stone quarried out of the ground and worked to suitable dimensions. It is also necessary in order to be comprehensive and strictly up to date to narrow the consideration even further and omit all references to the natural abrasives such as emery and corundum. We are, therefore, in this paper dealing only with the artificial abrasives, except where it is necessary to mention the natural ones as a matter of comparison.

All grinding wheels are composed of two main constituents:

1. *The Abrasive.* This is in grain form, the sizes of the grain depending upon the use to which the wheel will be put.

2. *The Bond.* This is a name used to indicate the material or substance by means of which the particles of abrasive are held together. In other words, the bond serves as a setting for the abrasives, and in this manner the face of a grinding wheel presents a more or less constant distribution of cutting particles.

Vitrified Wheels: The commercial method of classifying grinding wheels is by the kind of bonding material used. The most important type of wheel is the vitrified. The bonding material in this type is composed of various kinds of clay mixed together according to definite, secret formulas. A weighed amount of the abrasive, a weighed amount of the bond and a measured amount of water are all placed together in a mixing kettle, the whole thoroughly stirred for a definite length of time to insure uniformity, and then the mixture is drawn off from the bottom of the kettle into moulds and allowed to dry.

After the wheels have dried they are taken to a department known as the shaving department. Here the wheels are turned to the approximate dimensions and shape the order calls for.

Pressed Wheels: A certain variety of vitrified wheels is made by what is known as the pressed process. Here the bonding clays only have enough water added to them to make the particles stick together to a slight degree. The abrasive and bond are mixed in kneading machines, and after a uniform mixture is obtained, the mass is placed in an iron mould, uniformly distributed throughout the mould, and then the material is subjected to pressure by means of powerful hydraulic presses, the number of pounds per square inch being dependent upon the grade of hardness desired. After pressing, these vitrified wheels do not need shaving, but can be placed directly in the kilns for heat treatment.

Heat Treatment: The next operation in the manufacture of vitrified wheels is the heat treatment in the kilns. The object is to submit the abrasive and dry clay to a heat which will properly vitrify and mature the bond. The highest temperature reached is about the melting point of steel, and the length of time required for heating, the length of time held at high heat and the cooling period are very important.

The kilns are usually of the up and down draft, pottery variety, and are fired by a series of hard-coal fires placed equally around

the base of the kiln. The most common type of kiln is the single stack, natural draft, although some are in use which lead to a central stack.

After the kiln has cooled sufficiently the wheels are taken out, or unloaded, as the men in the factory say.

Silicate Wheels: In this class of wheels, as the name indicates, the bonding material is a silicate. A commercial grade of silicate of soda, commonly known as water-glass, is the main constituent and to this are added certain chemicals to make the bond waterproof. A weighed amount of the grain and a measured amount of the bonding material are placed in long cylinders, and these are slowly revolved end for end until a uniform mixture is obtained. The mixed mass is placed in an iron mould of the approximate dimensions the order calls for and rammed into place by means of hand hammers or air hammers. This is a rather delicate operation in that the personal equation enters to quite a large extent. After sufficient ramming, the wheel is placed, while still in the mould, in an oven heated by means of an ordinary coal fire. After the baking treatment the wheels are hard, and from here on they are treated the same as any other type.

Elastic Wheels: This name is derived from the fact that the bonding material has quite a degree of elasticity. The main constituent of the bond is of organic nature, the most satisfactory material being shellac. To this is added certain chemicals to facilitate hardening in the baking and also to make the wheel waterproof. A weighed amount of the grain and a weighed amount of the bond, containing the shellac in flake form, are placed in mixing machines, similar to the ordinary power bread mixer, containing kneading paddles. After the mixing process the whole mass is dumped out into a large shallow pan and allowed to cool, in which condition it is brittle. This brittle cake of abrasive and bond is broken up into small pieces and then put through a series of rolls which break the mass up into the individual grain. The rolls do not fit close enough, however, to reduce the size of the grain, the idea simply being to produce a mass composed of loose grains, each of which has a coating of shellac. In this form the material is placed in an iron mould

the approximate shape of the wheel, the mould and all are placed in a steam box and heated up to the temperature where the shellac is again of a workable consistency. In this condition the abrasive and bonding material is subjected to pressure in a heavy press, the number of pounds per square inch depending upon the degree of hardness desired. After this pressing operation the mould and all is again placed in another steam box and heated for a length of time which will permit the bond to become permanently hard. From here on this type of wheel is treated exactly the same as any other.

Vulcanized Wheels: Here again the name is indicative, the bonding material being rubber. The manufacture of vulcanized wheels is almost the same as that of any other hard-rubber product. A weighed amount of the very best grade of crude rubber, the right proportion of sulphur, and a weighed amount of grain are thoroughly mixed together by numerous passes through horizontal rolls so located that the material passes down in a vertical direction. After a uniform mixture is obtained, the mass is again passed through a set of rolls, this time so located that the material passes through in a horizontal direction. It is rolled down to the desired thickness, cut out to the desired diameter, and a hole of the desired diameter is also cut out in the center. The next operation is vulcanizing, and the vulcanizing of rubber wheels does not differ from the vulcanizing of any other rubber product. From here on, this type of wheel is also treated the same as any other.

Truing and Bushing: The next operation is that of truing, namely bringing the wheels to the true dimensions called for on the order. The wheels are mounted in a three-jaw chuck, revolved, and special tools resembling an emery wheel dresser brought up against the side of the wheel.

In order to bring the wheels to the desired diameter they are firmly held to a revolving arbor and the dressing tool passed back and forth across the face, gradually reducing the wheel to the desired size. For fine wheels which must be carefully shaped on the face, a diamond is used. This is mounted securely in a fixture and the diamond slowly passed across the face of the wheel,

light cuts only being taken, as otherwise there would be a tendency to crack and destroy the diamond.

In this department the bushing, as it is termed, is also placed in the wheel. This consists of lead, except where experience has shown that it is advisable to use a harder material, in which instances babbitt is used. The wheel is allowed to rest on its side in a three-jaw chuck, carefully centered, then a steel arbor from 0.002 to 0.005 inch (0.05 to 0.13 mm.) larger than the desired hole in the wheel, is placed in the center hole in the chuck and the lead then poured around the arbor. The lead solidifies in a few minutes, when the wheel is removed from the chuck, and the arbor is carefully driven out with a soft hammer. The bushing is then trimmed, so that it does not extend quite flush with the sides of the wheel. This is to provide clearance so that when the wheel is mounted on the machine there will be no possibility of the holding stresses being concentrated at the hole of the wheel.

Speed Test: The next operation in the manufacture of wheels is revolving at a speed higher than the wheel is recommended to operate, in order that the manufacturer may know that his product goes out with sufficient factor of safety. The testing speed for wheels is 9,000 surface feet per minute (2,700 m.) except those of organic bonds which are tested at a somewhat higher speed. Since wheels are recommended to operate in the neighborhood of 5,000 surface feet per minute (1,500 m.) this gives a factor of safety, based upon the square of the speed, of between three and four. A careful record of every test is kept, and before filing the men making these records are required to go before a justice of the peace and swear that their statements are true and correct. When a wheel has successfully passed the speed test and the records of the testers have been inspected, the manufacturer has gone as far as he can in assuring the trade that they are receiving a product which is safe to operate.

Final Inspection: The wheels next pass through a department where they receive final inspection. Here care is used to see that the right wheels are going to the right customer and that dimensions and other specifications called for by the order have been exactly complied with.

Packing and Shipping: The wheels are held rigidly in position in boxes or barrels by means of tightly rammed sawdust. Wheels go directly from here to the freight cars and are shipped to destination.

Grading: Grade is the word used to designate relative hardness of any given wheel. Different methods are in use of indicating grade, although the most common is to use the letters of the alphabet. One company uses the first letters of the alphabet for the harder grades, the middle letters for the medium grades and the last letters of the alphabet for the softer grades. Another company uses just the reverse of this method while others use a system based upon some particular word.

Grade is determined by measuring the resistance which a wheel offers to the penetration of a small steel tool resembling a screw driver. The wheels coming through process are compared with wheels of known hardness so that all variable factors are reduced to a minimum.

Since one of the important steps in the manufacture of grinding wheels is a heat treatment, a quantity of wheels all heat treated at the same time will vary somewhat in hardness. This becomes evident by a consideration of the fact that the individual parts of any lot of material which is heat treated, for example a lot of automobile gears, will vary somewhat after being hardened. It is therefore necessary to test after hardening, by means of a sclerescope or some other instrument, to be sure gears are not passed which are too hard or too soft. Those coming within a certain range of hardness can be used satisfactorily.

The belief is quite common that a grade is an exact value. This belief can probably be traced back to the wheel manufacturer endeavoring to educate *his* trade to the state of mind whereby it will be believed that competitors' wheels may vary in grade, but his will not.

A grade is not an exact value, it is a *range between limits,* and all wheels which come within this range are of one grade and carry the same grade letter.

A lot of wheels, all of the same dimensions, the size of grain, but different grades, were slowly speeded up to a point where centrifugal force became greater than the hardness of the wheel and breakage occurred. The number of pounds per square inch

tensile strength to which each wheel was subjected at the time of breakage was calculated by using a formula. The figures given in Figs. 1 and 2 should not be taken as exact, because formulas for centrifugal force in grinding wheels vary somewhat, but the figures will do for the purpose of comparison.

Fig. 1 illustrates the popular conception of grinding wheel grade, namely, that it is a definite value. For instance, take grade L. Reading on the left-hand side of the line, we see that

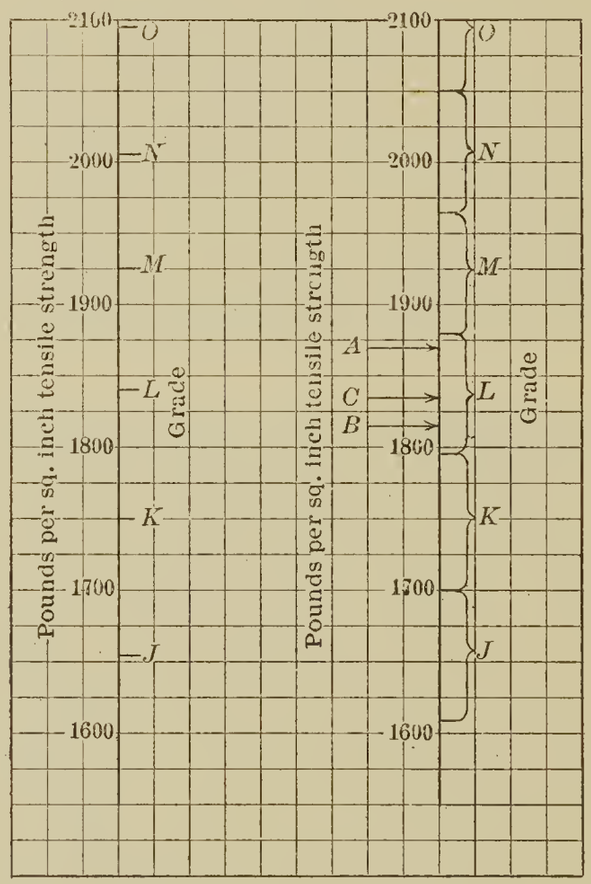

Fig. 1. Fig. 2.

1,840 pounds per square inch tensile strength is directly opposite. The statement is often made that it is a physical impossibility for the wheel manufacturer to exactly duplicate grades, in that the wheels will come plus, that is slightly harder, or minus, slightly softer, than grade desired. Statements of this kind are based on the conception illustrated in Fig. 1.

Fig. 2 gives more nearly a true representation of the facts in the case. Here it will be seen that grade L embraces a range of value between limits, the limits as calculated being 1,795 pounds per square inch (1.25 k. per sq. mm.) as the soft limit and 1,880

pounds per square inch (1.32 k. per sq. mm.) as the hard limit. A wheel of a tensile strength between these limits is truly a grade L. Likewise *all* grades are a range between limits.

This explanation may possibly assist in understanding the reason why wheels of the same grade, for example, two grade L wheels, may vary quite noticeably in a grinding action. Consider one wheel almost soft enough to be grade K and another almost hard enough to be grade M, as shown by the arrows A and B in Fig. 2.

Assume a certain grinding operation is being performed, all the variable factors of which, such as speed of work, speed of wheel, depth of cut, kind of material, etc., combine to bring a pressure against the wheels represented by arrow C. The wheel represented by arrow A will have long life while the wheel represented by arrow B, not being strong enough to stand up under the pressure of the operation, wears away quite rapidly, in fact very much more rapidly than the difference in hardness would seem to indicate.

GRINDING CHARACTERISTICS OF VARIOUS ABRASIVES.

Probably the most important physical property of an abrasive is hardness. Other properties such as toughness and ability to resist shock are also important, but knowledge of the art of grinding has not advanced sufficiently far so that we can definitely state the relative importance of the different physical characteristics; that is, we cannot state upon which of the properties the grinding action of the abrasive most depends. We know that the artificial abrasives are harder than corundum but not as hard as diamond. It is extremely difficult to determine differences in hardness of the artificial abrasives and for this reason we are sometimes led to believe that hardness is not so very important. This is because there is wide difference in the grinding action of existing abrasives and but little difference in hardness, as determined by present methods. However, if the hardness of mineralogical materials could be brought down to a satisfactory basis where variation could be measured in units of uniform size, we would probably find that there is as much variation between nine and ten on "Mohs" scale as there is between one and nine. Hard-

ness has been determined with sufficient accuracy, however, to make it possible to give the following statement with confidence.

Carbide of silicon abrasives are harder than aluminous abrasives.

When a grinding wheel containing a certain abrasive, satisfactorily grinds very tough material, we say the particular abrasive is possessed of considerable toughness. Whether or not this is the right word to use this paper will not discuss. Until the experiments which are being continually conducted have proved otherwise, the trade will continue to refer to this characteristic of abrasives as toughness.

We can readily conceive of two different materials, one of which is possessed of the properties of hardness and brittleness, while another may be less hard and tough. The brittle material may have sufficient strength to stand up under relatively light pressure, while the other material possessing less hardness but being more tough, may wear away so rapidly, due to its lower hardness, that the desirable property of toughness becomes entirely secondary.

Under other conditions we might have pressure brought to bear against the brittle material which it could not withstand, thus causing excessive wear, while the tough material, even though of lesser hardness, nevertheless is hard enough to stand up under this pressure for a sufficient length of time to be considered satisfactory.

The theory outlined above is quite frequently used to explain the marked difference in grinding action between the aluminous and carbide of silicon abrasives. Actual experience has shown that when materials of low tensile strength such as cast iron, brass, bronze, etc., are ground, carbide of silicon, which is hard but relatively weak, is more efficient than the aluminous abrasives. On the other hand, when grinding materials of high tensile strength, ranging all the way from medium carbon to the high-speed steels, we find that aluminous abrasives give better satisfaction than carbide of silicon.

Research is continually being conducted to bridge the gap between the two abrasives. Success is already accorded in the aluminous group. A material which is on the market and which carries the trade designation of 38 alundum, is better adapted for

grinding certain kinds of steel than the original material which is known as regular alundum. This latter material, however, is better than the No. 38 material on certain classes of work. Other varieties of aluminous abrasives come somewhere near these two but enough difference exists to be a sales factor. There is still a big field for research, and the manufacturers of artificial abrasives are very active and there is every promise of new varieties being soon on the market.

THE GRINDING WHEEL AND GRINDING MACHINE IN THE MANUFACTURE OF AUTOMOBILES.

The statements under this head must in the main be general, first on account of the limited amount of time, and in the second place, because quite frequently history is made in the automobile business between the time an article is sent to the printer and it is ready for distribution.

The following are important parts which depend upon the modern grinding wheel and grinding machine for the accuracy demanded:

Crankshafts.	Rear Axle Housings.
Piston Pins.	Worm Gears.
Piston Rings.	Spline Shafts.
Pistons.	Push Rods.
Cam Shafts.	Valves.
Eccentric Rods.	Bearings, both ball and roller.
Steering Knuckles.	

This list is not by any means complete. To mention all the parts of an automobile that come in contact with the grinding wheel would be to name almost every essential part, the possible exceptions being the sheet metal fenders, hood over the engine, radiator and the rubber tires; even the glass windshield, the springs in the cushion, enameled number plate, the clutch and brake pedals and the button to the Klaxon horn are ground.

The grinding wheel also has what may be called an indirect bearing on the manufacture of automobiles. The metal tools used in lathes, planers, boring mills, milling machines, and so forth, must be sharpened when they become dull. A great many of these tools are made of alloy steel which can only be satisfac-

torily shaped by using a grinding wheel. Stellite is a material which is rapidly coming into use. It, too, depends upon the grinding wheel to shape it as desired. When we consider this phase of the subject the importance of the grinding wheel is strongly emphasized and warrants one making the statement that present-day production would be only a dream if it were not for artificial abrasives.

There is a type of grinding machine known as the precision grinding machine. The word precision is used because machines of this type must be capable of producing work of great accuracy. The art of precision grinding has advanced very rapidly during the past few years, and the demand of the automobile manufacturer should get credit for a large share of the advance. Only a few years ago any one advocating the accurate grinding of shafts five inches to six inches long without table or wheel traverse would have been condemned as too visionary. This step in the art has long since been passed.

It is now possible to grind more than one diameter at one time with one wheel. This is an outgrowth of the use of very wide wheels taking extreme cuts without any traverse of the table or the wheel.

A conception of the refinement necessary in the modern grinding machine will become evident by considering the following:

A machine using a very wide wheel, say 10 inches or 12 inches, must have great rigidity as well as be capable of producing refined work. Imagine the forces present when a wheel weighing 150 or 200 pounds (68 to 90 kilos) revolves on a spindle in plain bearings at 1,000 to 1,200 revolutions per minute. There must be accuracy to keep this spindle in perfect alignment so that the face of the grinding wheel will produce an absolutely straight cylinder, and the weight required in the base of the machine and the wheel slide to absorb all vibration caused by the revolving mass must be ample. Another factor which must be borne in mind is the resistance which is offered when the wheel is brought in contact with the work, as small particles of a very hard material are removed at an extremely rapid rate. It has been calculated that on a wheel 24 inches (60 cm.) diameter and 4 inches (10 cm.) wide there are 1,860,171,000 cutting particles coming in contact with the work each minute. The spindle bearings must be so

closely adjusted that the boxes will be quite hot when the machine is in operation, in fact a temperature of about 140° F. (60° C.) is desirable.

Limits on the work being ground of 0.0005 inch (0.013 mm.) are very common, those of 0.00025 inch (0.006 mm.) quite common, and in some cases requirements are so exacting that less than 0.00025 inch (0.006 mm.) is demanded. It should also be borne in mind that when the work is reduced 0.00025 inch (0.006 mm.) the massive slide carrying the wheel spindle and the grinding wheel moves forward only half of this distance. If it were possible to split a piece of tissue paper into 12 thicknesses, the thickness of one of the resulting pieces would represent the motion of the wheel slide when the grinding wheel removes 0.00025 inch (0.006 mm.) from the work. Bear in mind that this accuracy must be maintained not only where very small cuts are taken but also under conditions where the object is to grind off as many cubic inches per minute as possible.

Many more interesting points could be given but it is hoped the few mentioned above are sufficient to have awakened a sense of appreciation of the modern grinding wheel and grinding machine.

The next time you look at the engine and transmission machinery in your car do so with a certain amount of reverence, and take a few moments from your busy life to reflect that a product of the electric furnace has made all this possible—the artificial abrasive.

The Norton Company,
Worcester, Mass.
March 21, 1917.

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 5, 1917, President FitzGerald in the Chair.

THE ELECTROLYTIC PICKLING OF STEEL.

By M. De Kay Thompson and O. L. Mahlman.

[*Abstract.*]

The object of the following investigation was to test the relative efficiency of the electrolytic and the chemical processes of pickling steel, as regards the amounts of acid, iron, and time consumed. The electrolytic method is found superior in all three respects.

INTRODUCTION.

All the iron or steel objects which in the process of manufacture have been heated in the air are covered with "fire scale," which is an oxide of iron corresponding in composition approximately to the formula Fe_3O_4. This has to be removed before the surface can be plated or galvanized, and this is usually accomplished by immersing in some acid until the scale is removed by the hydrogen formed by the action of the acid on the iron beneath the scale, which it reaches through the cracks in the scale.

The action which would be expected if a sheet of iron covered with scale were used as cathode in an acid solution is a reduction of the higher oxide to lower oxide. This oxide would be dissolved by the acid. There would also probably be a certain amount of chemical action between the iron under the scale and the acid, as in the purely chemical treatment. It is this action which the electrochemical process attempts to avoid as much as possible.

The electrolytic method has been patented by C. J. Reed (U. S. Patent, Nos. 855,667, 827,179, 827,180 (1907). See also Tr. Am. Electroch. Soc. **11**, 181, 1907, and Hering, Met. and Chem. Eng. **13**, 785, 1915). His specifications, which are followed in this investigation, are: sulphuric acid of 1.2 specific gravity, at 60° C., current density of 40 to 60 amperes per square foot (4.27 to

6.42 amperes per square decimeter). The anode is lead. The iron sulphate formed is to be removed from the solution from time to time by cooling to 0° C.

EXPERIMENTAL.

The method of comparing the two operations consisted in treating two similar mild steel plates covered with equal amounts of scale by the two methods until their appearance showed the pickling was completed. The pickling baths were then concentrated until all solid matter which had dropped off was dissolved, and were then analyzed for iron. The amounts of iron dissolved in the two processes formed the basis of comparison.

A comparison that would probably represent more nearly the conditions of practice would be to filter off the solid matter and determine the iron in solution right after the pickling. The method given above was adopted because it was thought the results would be more consistent.

The scale was produced by heating for 2 to 8 minutes pairs of plates in a muffle furnace, after which they were cooled in air. One of these was then treated by the chemical method, the other by the electrolytic.

The chemical treatment consisted in immersing in a boiling sulphuric acid solution containing about 5 percent acid until the surface was cleaned of scale. The cell for electrolytic pickling was placed in a thermostat and the iron plate was suspended between two lead anodes. A weighed portion of the concentrated solutions were taken for analysis. The iron was determined by passing the solution through a Jones reductor and titrating with potassium permanganate.

The following three runs were made:

TABLE I.

	Electrolytic	Chemical
Area of plate (sq. cm.)	152	152
Strength of acid	1.2 sp. gr.	4%
Duration of pickling (minutes)	19	23
Temperature	62°C.	100°C.
Current (amperes)	8.5	
Volts	2.5	
Total weight pickle liquor (grams)	647.3	708.6
Weight analyzed (grams)	32.56	42.61
0.2n$KMnO_4$ used (c.c.)	14.28	23.10

TABLE II.

	Electrolytic	Chemical
Area of plates (sq. cm.)	823	830
Strength of acid	1.2 sp. gr.	4%
Duration of pickling (minutes)	32	41
Temperature	60°C.	100°C.
Current (amperes)	9.5	
Volts	2.7	
Total weight pickle liquor (grams)	919	470.3
Weight analyzed (grams)	56.05	35.20
0.2nKMnO$_4$ used (c.c.)	30.47	63.85

TABLE III.

	Electrolytic	Chemical
Area of plates (sq. cm.)	832	835
Strength of acid	1.2 sp. gr.	5%
Duration of pickling (minutes)	3.75	43.5
Temperature	60°C.	100°C.
Current (amperes)	9.4	
Volts	2.6	
Total weight pickle liquor (grams)	755	507.7
Weight analyzed (grams)	30.81	30.13
0.2nKMnO$_4$ used (c.c.)	8.39	17.65

The appearance of the surfaces of the plates from the two processes was the same. The results are given in Table IV for comparison.

TABLE IV.

Run Number	1	2	3
(a) g. iron per sq. cm. in electrolytic pickle	0.0166	0.00678	0.00275
(b) g. iron per sq. cm. in chemical pickle	0.0282	0.0115	0.00395
Ratio of (a) to (b)	0.590	0.590	0.696
Watt hr. used per sq. dm. pickled	4.42	1.65	0.184
Watt hr. per g. iron in electrolytic pickle	2.67	2.43	0.667
Cost of power for removing 2,000 lbs. of iron (as scale and iron)	$7.44	$6.76	$1.86
Value of acid saved for every 2,000 lbs. of iron removed	25.00	25.00	15.70
Value of saving in iron for every 2,000 lbs. of iron	55.60	55.60	34.80

(Power was figured at $20 per horse power year, acid at 80 cents per 100 lbs. 60° acid, iron at 4 cents per pound).

From this it is evident that under these assumptions the saving in iron and acid is far greater than the cost of the power. Part of the iron included in this calculation is the scale itself, as explained above. These experiments should be repeated, determining only the iron in solution and not including the scale which is removed as such during the pickling. The values of practice would then lie between these two values. In these experiments probably more acid is consumed than would be used in practice, because in practice not all the scale would be dissolved.

Run 3 is seen to vary considerably from the other two runs, probably due to accidental differences in the quality of the scale. A larger number of runs would be desirable in order to get a better average value in the saving which could be effected by the electrolytic method.

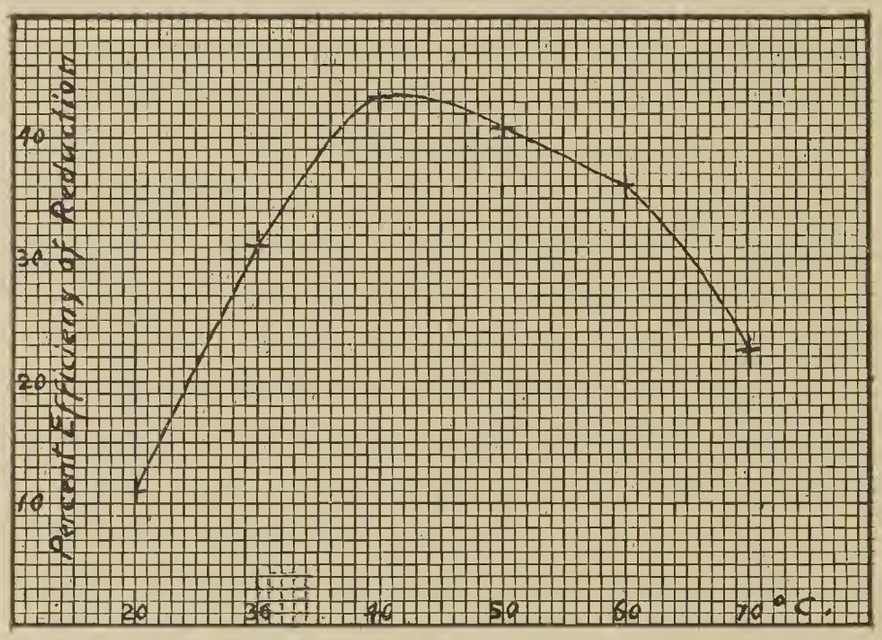

FIG. 1. Relation between temperature and efficiency of reduction of Fe_3O_4 at 5.4 amperes per sq. dm. (50 A. per sq. ft.).

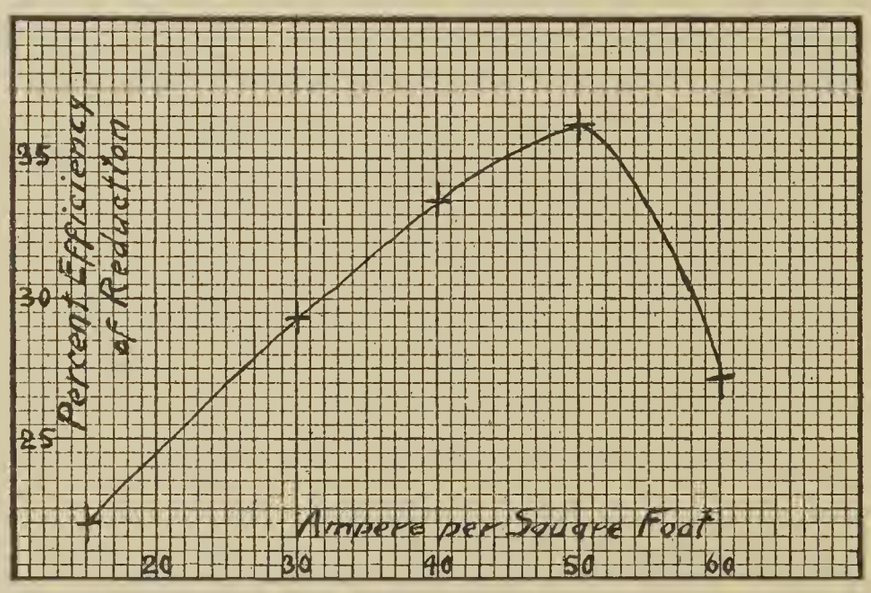

FIG. 2. Relation between current density and efficiency of reduction of Fe_3O_4, at 60° C.

In order to see to what extent the oxide Fe_3O_4 is reduced by the current when acting as cathode, some fused magnetite electrodes 3.80 cm. in diameter were used as cathodes in a solution of sulphuric acid of 1.2 sp. gr. enclosed in a porous cup, having

a gas-tight cover through which the hydrogen liberated passed to a collecting bottle. It was then transferred to a Hempel burette for measuring. A gas coulometer was connected in series with this cell and the gas was collected in a eudiometer tube. The collection from the two cells was made for equal simultaneous intervals. By comparing the amount of hydrogen liberated in the coulometer (⅔ of the total gas) with that liberated from the cathode compartment, the percent of hydrogen used to reduce the oxide can be computed.

The results are given in Table V, and Plots 1 and 2.

TABLE V.

Current Density Amperes per Sq. Ft.	Temperature C°	Coulometer Vol. cc.	Vol. H_2 cc.	Eff. Percent
60	60	142.7	68.4	28.0
60	60	144.4	70.0	27.4
60	60.5	144.5	71.0	26.3
50	60	146.2	62.4	36.0
50	60	146.2	62.4	36.0
50	60	144.0	61.0	36.5
40	60	139.7	61.8	33.5
40	60	140.0	62.0	33.5
30	60	145.4	66.8	31.1
30	60	145.4	68.0	29.9
30	60	145.8	71.0	27.0
15	60	102.7	53.2	22.2
15	60	102.3	53.1	22.1
50	20	121.0	71.8	10.9
50	20	120.2	71.4	11.0
50	30	102.1	46.0	32.4
50	30	101.7	46.4	31.6
50	30	101.0	47.0	30.2
50	40	102.4	34.0	50.2
50	40	101.8	38.8	42.8
50	40	103.0	43.0	37.4
50	50	123.8	48.8	40.9
50	50	123.8	48.8	40.9
50	60	146.2	62.4	36.0
50	60	146.2	62.4	36.0
50	60	144.0	61.0	35.5
50	70	102.8	53.4	22.0
50	70	102.5	53.8	21.2
50	70	103.3	52.2	24.2

The curves show that the reduction is most efficient at about 50° C. and with a current density of 50 amperes per square foot.

SUMMARY.

1. The relative efficiency of electrochemical and chemical pickling was determined, and the saving in expense which would be effected under the conditions of these experiments, showing greatly in favor of the electrochemical method.

2. The extent to which fused magnetite is reduced in sulphuric acid solution under different conditions of temperature and current density was also measured, and the best conditions of temperature and current density were determined.

Electrochemical Laboratory,
Massachusetts Institute of Technology,
Cambridge, Mass.
September, 1916.

DISCUSSION.

CARL HERING[1]: Had I known in advance about these tests by Thompson and Mahlman, I would have suggested certain modifications. They unfortunately used very highly oxidized samples, judging from the time specified in two of their test runs; my own tests were made under commercial conditions of oxidation, such as occur in the annealing of sheets and wires, and show that the cleansing by the electrolytic method could be done generally in about thirty seconds, and in some exceptional cases forty to ninety seconds. Exactly the same sheets were used that are now being pickled commercially in very large quantities by the old method requiring ten to twelve minutes, and some sheets must be pickled twice. Some of the samples referred to in the present paper were therefore evidently over-oxidized.

The chief advantage of the electrolytic process lies in the saving of the good iron and the acid which are consumed unnecessarily by dissolving the iron underneath the scale. The scale itself is not dissolved chemically; the only way it can be dissolved is to generate an electric current which reduces the oxide to a lower one which will then be dissolved. In the ordinary pickling pro-

[1] Consulting Electrical Engineer, Philadelphia.

cesses this current is generated by the expenditure of good iron and acid, constituting a primary battery; this current develops the necessary hydrogen which reduces the higher oxide. In the electrolytic process this current is produced by a dynamo, and I think we all know that it is much cheaper to produce a current by the dynamo than by dissolving iron in sulphuric acid, although the latter is the way it is done today in all large steel pickling plants.

In large installations this saving of acid and metal is very important. It is much greater than any one has any idea of until he has made the actual determinations. I based my estimate on samples obtained from the makers of steel sheets, and found it ran into hundreds of dollars a day, which is a large amount of waste, even for a large company.

The other advantage of the electrolytic method is the thoroughness of it. You can keep a sample in the bath a long enough time to get out the last trace of oxide from the deepest pits, without consuming any of the metal itself. By the old method steel tubes are sometimes eaten through so badly that they lose their strength, owing to the fact that they had to be left in the pickling solution so long to get at the deeply-seated oxide. With the electrolytic method no iron is dissolved, and you can keep the metal in the bath as long as necessary to get it thoroughly reduced.

As to the cost of the current, my tests show a cost of about 3.5 cents per thousand square feet of sheet covered with the ordinary oxide formed in annealing ovens; not the scale formed in hot rolling, which is very much thicker. The cost of the current is insignificant as compared with the saving of the acid and good iron.

Another advantage is the smoothness of the surface, which is very important in tinning and galvanizing, as it saves considerable tin and zinc. I have looked at the surfaces under the microscope and found them to be very unlike, which observation does not agree with that of the authors of the paper. In pickling by the electrolytic method (if done correctly) the surface will be almost polished if it was practically polished before oxidation; the surface pickled by the ordinary process looks more like velvet, being full of tiny pits which must be filled with zinc or tin when subsequently galvanized or tinned.

The cost of pickling in the usual way is probably about five dollars a ton, and even if only half of that amount could be saved it is evident what it would save for large plants.

The authors lay considerable stress on the efficiency, and find figures for the best conditions slightly different from those given originally by Mr. Reed. I would like to call attention to the fact that the curves refer to current efficiencies, but as the current is so cheap in this process, it seems to me the most efficient use of the current is decidedly not a criterion for judging the economy of the process. The true criterion is getting the work done as quickly and thoroughly as possible, and with the least labor cost and least loss of iron and sulphuric acid, that is, at the least total cost; if it can be done quicker it will take less plant and, therefore cost less than if a little more current is wasted. I cannot therefore agree with the authors that the efficiency curves given by them are a criterion. For one large concern I figured out that the waste in ordinary pickling reaches about a half million dollars a year.

I brought with me a sample of a commercial sheet, just as it is obtained from the makers. One end of this sheet was pickled electrolytically and the other by the ordinary process. The end which was pickled by the ordinary process required sixteen minutes, and if you will look at it you will see it is very rough and looks very badly; the end which was electrolytically pickled required one minute, and you will see how nicely smooth it is. I also have a little sample here of a piece of nickel-iron pickled electrolytically on one end; also some pieces of wire, half of which are the original oxidized wires and the other half those that have been electrolytically pickled.

E. F. ROEBER[2]: Did the concerns which could save half a million dollars a year adopt the process?

CARL HERING: It is not yet in extended use, though under consideration. A demonstration plant of commercial size is now being erected. Anybody can convince himself very readily concerning the process. At present we are working out the details for handling a large tonnage.

[2] Editor, Metallurgical and Chemical Engineering.

J. W. RICHARDS[3]: I would ask Dr. Hering whether he has had any experience with the relative increase in brittleness of thin sheet pickled by the two methods. That, I understand, is an important matter in the pickling operation, and any process which would produce less brittleness would be advantageous on that account. If the process made thin sheet more brittle, from absorbed hydrogen, it would injure the prospects of its adoption.

CARL HERING: I have no data on that point, and can only say that in both cases hydrogen is evolved on the iron surface, hence I should suppose that neither is better or worse than the other in this respect.

W. H. ALLEN[4]: What is the effect of this process on the removal of oils and the more or less solid fats or soaps from drawing compounds?

CARL HERING: I do not know. Removing grease has no connection with the electrochemical action, but the solution is hot, 60 degrees Centigrade, and I should imagine that oils at that temperature and with that rapid evolution of hydrogen would probably be cleaned off. Grease spots on the surface do not seem to retard the reduction, hence I presume the process removes the grease. No attempt is made to clean the iron of grease before it is pickled in the usual way, so that I do not think that the grease would affect the new process in the slightest degree.

[3] Professor of Metallurgy, Lehigh University.
[4] Detroit Technical Institute, Detroit, Mich.

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 4, 1917, President FitzGerald in the Chair.

THE CORROSION OF CAST IRON AND ITS BEARING UPON THE ELECTROLYTIC THEORY OF CORROSION.

By E. A. Richardson and L. T. Richardson.

[*Abstract.*]

Cast iron has not been as extensively studied for its anti-corrosion properties as steel or pure iron. Being less pure and more heterogeneous than either of the latter, it should rust faster according to the electrolytic theory of corrosion. Three pieces of these three materials were exposed to rusting influences for seven months, then cleaned and weighed. Pure iron corroded least, cast iron 25 percent more, and steel 100 percent more. The electrolytic theory of corrosion does not explain these results.

In reviewing the literature relating to the corrosion of cast iron, one is unable to find any extensive references or data upon the subject. This is rather surprising when one considers the many scientific tests and observations that have been made upon the corrosion of iron and steel, the published results of which make an extensive and varied literature. The field of cast iron as regards its usefulness as a rust-resisting metal has been much neglected, and today remains almost unexplored.

This is due, no doubt, in part to the fact that only in the last few years has the resistance of irons to corrosion been considered as one of their important properties. The efforts to improve materials for structural and other purposes have been directed toward the production of a material having superior physical properties such as tensile strength and possessing a greater reliability. This is the reason that cast iron, which once was used extensively for structural purposes, was replaced by steel. How-

ever, for many other purposes, cast iron is still used in enormous quantities in places exposed to corroding influences. In view of this it is surprising that such little attention has been devoted to a study of the corrosion of this material.

Most of the published information relating to the corrosion of cast iron may be divided into two classes. The first consists of numbers of isolated instances where pieces of cast iron have endured for a number of years and seem to have been almost unacted upon by corrosive influences. The second class consists of actual tests in which attempts have been made to compare cast iron with iron or steel as regards its rust-resisting properties.

The information contained in the first class consists as a rule of isolated observations that have been made upon cast iron under actual service conditions, particularly relating to cast-iron pipe for conveying water underground. These observations will not be discussed, but the reader is referred to the original articles,[1, 2, 3] and especially one by Mr. M. R. Pugh,[4] which includes a very good summary of these findings. It will suffice to say that many instances are known where cast-iron objects have lasted many years, even centuries, and have remained in good condition when exposed to corrosive conditions, and that when used underground, cast iron is usually superior to other kinds of iron.

These observations are especially interesting as throwing some light upon the electrolytic theory of corrosion. This theory states that the more heterogeneous the material the greater the rate of corrosion of that material. While other factors should of course be taken into account, yet this seems to be the interpretation usually given to the electrolytic theory of corrosion. If this interpretation be true, then one would expect to find an increase in corrosion as the purity of the iron was decreased. For instance, pure iron, steel and cast iron should resist corrosion in the order named.

The second class of tests, namely those consisting of actual tests, seem to indicate differently, as may be judged from the following references:

J. N. Friend[5] tested grey cast iron and mild open-hearth steel by an alternate wetting and drying method, and found that cast iron was decidedly superior to steel.

Thwaite[6] collected in 1880 all available data upon the corrosion

of cast iron compared with that of wrought iron, and obtained for the relative corrosion the following results:

	Pure Air	City or Sea Air
Wrought iron	0.655	6.690
Cast iron	0.604	2.637
Cast iron (skin removed)	0.584	4.763

K. Arndt[7] measured the amount of oxygen absorbed by iron and steel in damp air, and obtained data as follows:

Days	C.c. Oxygen Absorbed		
	Cast Iron	Mild Steel	Wrought Iron
1	13	13	5
5	30	45	30
10	45	63	109
20	59	108	198
30	73	156	293
43	95	213	389

It is evident from the above table that cast iron rusts very rapidly at first, but the rate rapidly decreases, and in a very few days it becomes superior in resistance to either steel or wrought iron. Friend[8] in commenting on this test states, "This is quite in accordance with experience, for cast-iron articles have been repeatedly proved to offer a very high resistance to the corroding influences of time."

Burgess and Aston[9] tested several kinds of iron and steel under atmospheric conditions, among which were cast iron, steel and pure iron. They found the relative corrosion to be:

High purity iron	88.4
Steel	63.5 to 150
Cast iron	93.

They say, "Heterogeneity of structure of metals is generally supposed to be antagonistic to durability but this investigation shows that if it is a factor it is one of secondary significance and overshadowed by other factors."

It is evident, therefore, judging from the literature, that cast iron, in spite of its extreme heterogeneity, is very rust-resisting. The data upon this subject, however, being so meager, conclusions should not be drawn from results so radically different from the

predictions of such a widely accepted theory as the electrolytic until enough data are obtained to warrant doing so. The following test was therefore made in an endeavor to add to the information already obtained upon this subject.

For the test, three kinds of irons, typical of three stages of heterogeneity were chosen, namely: grey cast iron, a low-carbon steel and a commercially pure iron. By analysis, these materials contained the following impurities:

	Sulphur	Phosphorus	Manganese	Total Carbon	Silicon	Copper
Cast iron	0.059	1.02	0.48	3.26	2.40	none
Steel	0.030	0.006	0.33	0.10	trace	trace
Pure iron	0.021	0.004	0.015	0.015	0.005	0.025

In order not to depend entirely upon analysis as proof of heterogeneity, photomicrographs were also made. These are given below.

Cast Iron. Steel. Pure Iron.

It is evident from the analyses as well as from the photographs that a wide range of heterogeneity exists in these three kinds of iron, and according to the electrolytic theory the materials should corrode in the order: cast iron, steel, pure iron.

For the test, four test-pieces of each material were taken, were carefully annealed at 750° C., the effects of oxidation removed by filing and then accurately weighed. The pieces were all given exactly the same treatment and any factors such as the skin on cast iron were eliminated. These test pieces were placed in a wooden rack and exposed to the atmosphere.

The test was examined at intervals of about one week. At the

end of a month, visual observations indicated pure iron to be the best material as regards resistance to corrosion, while cast iron and steel seemed about equal although decidedly poorer than pure iron. Later on, the rate at which the cast-iron specimens were rusting decreased and at the end of about four months cast iron and pure iron were about the same, while steel was much poorer than either. This relative condition lasted until the end of the test.

At the end of seven months the test pieces were removed, cleaned with neutral ammonium citrate and carefully reweighed. The losses computed in grams per square centimeter were:

Cast iron	0.966
Steel	1.546
Pure iron	0.771

The specimens, after cleaning, were examined as to the condition of the surface, the depth of pits and the uniformity of the rusting. No difference could be detected between the cast iron and pure iron as regards these three points; in fact they seemed to corrode in very much the same manner. The steel was, on the contrary, very deeply pitted and the rusting on the surface had been very irregular.

The results of this test agree with other tests and add to the evidence already accumulated, that the resistance of an iron to corrosion does not necessarily depend upon its purity or homogeneity, as would be indicated by the electrolytic theory of corrosion. This theory, in its present accepted form, does not explain the great resistance offered by cast iron to corrosion. While it may be true that the initial rusting is largely electrolytic in character, other factors, such as the adherence of the rust and the protection thereby given to the metal, come into operation and outweigh any electrolytic corrosion—a conclusion that has also been arrived at by other observers.

BIBLIOGRAPHY.

1. Permanence of Steel and Masonry Construction. Discussion by J. F. O'Rourke. Amer. Inst. Civil Eng. (1902) **28**, 670.

2. Preservation of Materials. Discussion by C. C. Simpson. Amer. Inst. Civil Eng. (1903) **29**, 313.

3. The Rusting of Iron. J. Meehan. Nature (1916) **75**, 31.
4. External Corrosion of Cast Iron Pipe. M. R. Pugh. Amer. Inst. Civil Eng. (1915) **78**, 806.
5. The Corrosion of Iron and Steel. J. N. Friend. Journ. of Chem. Ind., June 15, 1915, p. 617.
6. Thwaite. Journ. Iron and Steel Inst. (1880) 667.
7. K. Arndt. Chemiker Zeit. (1910) **34**, 425.
8. The Corrosion of Iron and Steel. J. N. Friend. p. 102.
9. The Rate of Rusting of Iron and Steel. C. F. Burgess and J. Aston. Proc. 8th Int. Cong. of App. Chem., **26**, 453.

DISCUSSION.

CARL HERING[1]: The authors do not seem to take into consideration that there is silicon in cast iron, and silicon, which acts electrochemically like zinc and aluminum, would tend to protect iron electrolytically. I do not think that they interpret the theory of electrolytic corrosion correctly when they lay such stress on homogeneity. It seems to me it depends on what the other ingredient is. You could mix granules of iron and zinc together and get perfect protection of the iron, although it would be a very heterogeneous mass. On the other hand, one could make a homogeneous mixture which would not protect the iron at all.

W. L. BADGER[2]: It seems to me remarkable that so little of the work done on corrosion in this country takes notice of one of the most important pieces of work yet done on this subject. I refer to the paper of Heyn and Bauer on "The Corrosion of Iron in Water and Aqueous Solutions," in Mitteilungen aus dem Königlichen Materialprüfungsamt, **26**, pp. 1-104 (1908). In this paper are presented the results of a most comprehensive experimental study on corrosion, such as has never been undertaken before or since. It is quite inexcusable that papers on the corrosion of iron which append anything in the way of a bibliography should not contain a reference to this.

In the course of this work (including several thousand indi-

[1] Consulting Electrical Engineer, Philadelphia.
[2] Asst. Professor of Chemical Engineering, University of Michigan.

vidual experiments) a careful study was made of the exact conditions necessary to obtain comparable results in corrosion experiments. Heyn and Bauer showed that the conditions must be specified with the greatest exactness if the results of individual experiments in the same series were to have any significance at all; to say nothing of isolated experiments which could only have value by comparison with some one else's work. In the light of this it seems to me that a fault of this paper is that no details at all are given as to the arrangement of the individual experiments.

If more workers in this country would pay some attention to the results of this remarkable paper from the Prüfungsamt it might be that we would not have the mass of unrelated and entirely unintelligible data on corrosion with which our literature is burdened.

Heyn and Bauer made only one very limited series of experiments on cast iron. The results showed that in distilled water, tap water, and 1 percent NaCl solutions, the samples tested showed about the same amount of corrosion. Soft steel, wrought iron, and cast iron (the analysis of each sample is given in the original) showed a relative corrosion of 100, 101, and 107, respectively. To throw a light on the dilute H_2SO_4 test, often used to show the tendency of iron to corrode, the same three samples were tested in 1 percent H_2SO_4. Here the relative amounts of corrosion were 100, 200, and 10,000, respectively.

T. S. Fuller[3]: The authors of this paper speak of the bearing of heterogeneity on the theory of corrosion. Another example of this is the addition of a small amount of copper to steel. Some experiments were conducted several years ago by D. M. Buck, in which copper was added to pure iron in amounts up to 0.34 percent. It was found that this copper-steel resisted corrosion very much better than the ordinary steel. It seems to me that this is another case of heterogeneous substances resisting corrosion better than pure metal.

I believe that we may form a mental picture of the effect of the silicon in iron very much as we do of the effect of chromium in iron in resisting high-temperature oxidation. The oxide of chromium forms on the surface of the metal, and thus prevents

[3] Research Laboratory, General Electric Co., Schenectady.

further oxidation. May it not be in this case that we have silica formed on the surface of the iron-silicon alloys, or possibly hydrated oxide of silicon, which slows up the rate of corrosion?

F. N. SPELLER[4]: The small number of tests made by the author would hardly in themselves have a practical bearing on the question of the relative corrosion of these materials. Probably the authors did not intend that these few results should be used to draw any such conclusions, but rather intended them to illustrate what they evidently feel is a weakness in the electrolytic theory. However, in reading the record of this meeting, some may attach undue importance to the apparent good showing made by cast iron in these tests. I have recently had occasion to investigate this matter by going over a considerable number of tests on cast iron and steel and do not find any material difference in the loss per unit of area when the casting skin has been removed from the iron prior to exposure. In practice the casting skin often affords considerable protection, but is evidently not always to be depended on, as we can see by the fact that all cast-iron pipe is given a dip in coal tar before shipment.

As regards the effect of these conclusions on the electrolytic theory, I recall the paper by Heyn and Bauer which the previous speaker has referred to, and I believe Heyn and Bauer show very clearly, as have a number of others since, that composition has very little to do with the actual rate of corrosion; this, however, does not vitiate the electrolytic theory. In corrosion, the electrolytic theory stands regardless of the composition, for corrosion is a surface reaction, and the slightest difference in the surface condition, whether it is the difference of accidental finish, or composition, is enough to start corrosion, and once corrosion starts the products of corrosion produce on the surface a different potential, far greater than any other difference found in the metal itself. There is also the mechanical protection which may be afforded by such an element as graphite in pig iron. Cast iron is an extreme illustration of this protective action, as the graphite amounts to about fifteen percent of the volume of the metal, and is very strongly electro-negative to iron. The graphite has, undoubtedly, a considerable mechanical protecting influence, but it

[4] Metallurgical Engineer, National Tube Co., Pittsburgh.

also exerts a strong electro-negative action towards iron, and it is simply a question of the balancing of these two factors, as to which is going to predominate. Evidently these forces nearly balance each other, as the relative corrosion of cast iron and steel would indicate. We must bear in mind the common experience that cast iron does not always show the full extent of the damage due to corrosion. Very often the cast iron will be completely decomposed underneath the surface, and this damage will not be evident on the surface, so that you can quite readily cut a piece of apparently solid metal with a knife. Quite frequently I have found water and gas mains preserving their form with very little of the metal left, and this condition is only revealed by some accident, such as settlement of the soil.

I recall a recent case of a gas main in the vicinity of Boston, near the seashore, where the pipe had been in the earth only five or six years. About a year ago the line failed and had to be taken up for replacement; it was found that the metal was entirely destroyed by the sub-surface corrosion.

I do not see anything in this paper that throws discredit upon the electrolytic theory. Copper-steel has been mentioned, and here the longer life seems to be due to the formation of an oxide which adheres very tenaciously to the surface of the iron. Copper-steel and ordinary steel in the atmosphere act very much the same for the first few weeks, after which the corrosion of the copper-carrying steel is retarded very materially, and in some cases actually seems to stop.

C. F. BURGESS[5]: I agree with the former speaker that we ought not to allow to stand unchallenged the statement that comparatively little attention has been given to the corrosion of cast iron. In fact, there is probably no one phase of the corrosion problem that has been investigated more, and the object of so much litigation, or caused more trouble, than the electrolytic corrosion of cast iron.

There has been a great deal of work done in a somewhat unscientific way in the study of corrosion of underground mains, and Mr. Speller has pointed out some of the peculiar conditions of such corrosion.

[5] Burgess Laboratories, Madison, Wis.

D. L. MATHIAS[6]: I have analyzed the coating formed on a piece of cast iron undergoing acid corrosion, and found the coating consisted almost entirely of silica and graphite. I have also made several tests on the loss in weight per unit of area, over a certain length of time, and have discovered that the action is rather slow at first, then increases, probably because etching pits are formed which increase the area exposed to the action of the acid. The rate of corrosion then falls off rapidly as the protective coating of silica and graphite forms.

J. L. SCHUELER[7]: With regard to copper in steel, when you dissolve copper-steel in nitric acid the first thing that goes into solution is copper, and I wonder whether there is not some other explanation for the fact that copper protects steel from corrosion.

Why is it that when you allow any kind of a steel to corrode to destruction, that the corrosion takes place in layers and not in craters, as one would believe from this paper? It always takes place in the same direction in which the material has been rolled.

W. L. BADGER: In regard to the point made by the last speaker, as to local corrosion as opposed to corrosion in uniform layers; in Heyn and Bauer's paper experiments are recorded in which, in certain electrolytes, the corrosion proceeded uniformly over the whole test piece, while in other electrolytes the corrosion would be strongly localized. If I remember correctly, the localized corrosion was strongest in alkaline electrolytes.

The question of whether or not the corrosion is localized is apparently partly dependent on the nature of the electrolyte and also, partly, a question of the surface conditions on the test pieces.

H. M. HOWE[8]: The electrolytic theory of corrosion ought not to be expected to dispense with the need of applying other considerations. The good resistance of cast iron in spite of its heterogeneity need not conflict in the least with that theory, when we remember the enormous advantage which this substance has in being crossed with plates of graphite, which may well form a great obstacle to the progress of corrosion, and thus outweigh the greater heterogeneity. In the same way the sheets of cinder

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[7] Chemist and Metallurgist, Keystone Steel & Wire Co., Peoria, Ill.
[8] Consulting Metallurgist and Author, Bedford Hills, N. Y.

in wrought iron explain readily why that very heterogeneous material resists corrosion so well. This explains readily the Arndt results quoted by the authors on page 193. The greater heterogeneity of the cast iron leads to faster initial corrosion. But as this proceeds the receding surface leaves bare progressively increasing surfaces of graphite sheets, which in themselves resist corrosion strongly. It is as if initially internal surfaces of paint were gradually exposed by the removal of the metal initially overlying them. This principle was elaborated by me in 1900.[9]

Though I have shown that these apparent flakes of graphite are rather to be regarded as graphite fillings within a very fine skeleton of ferrite, their action in impeding the progress of corrosion is readily understood. The individual threads of ferrite in this mass are so extremely fine that corrosion could not readily pass along them.

The plates of cementite and the masses of eutectic in white cast iron should have a retarding effect, like that of graphite in gray iron and of cinder in wrought iron.

What may be called the mechanical principle in corrosion may be enunciated thus: The presence of sheets of a resistant constituent, whether macroscopic or microscopic, offers a mechanical obstruction to corrosion, the influence of which increases as corrosion proceeds, thus leading to a continuous retardation of the corrosion.

J. L. SCHUELER: I referred more to steel which had been allowed to corrode to destruction in the atmosphere, without any so-called acid corrosion test.

W. L. BADGER: The tests to which I referred were all made in either solutions of electrolytes or in water. There were no tests under atmospheric conditions.

D. L. MATHIAS: I have found, in my experiments on acid corrosion of iron and its alloys, that an addition of from one-quarter to three-quarters percent of chromium will greatly increase the acid-resisting qualities of cast iron. Chromium favors the formation of cementite, which offers considerable resistance to corrosion.

[9] The Relative Corrosion of Wrought Iron, Soft Steel, and Nickel Steel. International Congress on Testing Materials of Construction, Paris, 1900; Engineering and Mining Journal, August 18, 1900.

J. W. RICHARDS[10]: Dr. Hering has remarked that the silicon in the cast iron may be a protecting agent, which preserves it from corrosion, and I think that probably strikes at the root of the problem.

In Mr. Kowalke's paper, discussed previously, it was shown that an alloy containing 2.5 percent silicon corroded much slower than a specimen with 1.2 percent silicon; an increase of 1.3 percent of silicon diminished the corrosion 70 percent.

I believe the electrolytic theory as explained by Mr. Badger also explains very clearly the reason for the protective action of the silicon. Hydrated silica is formed by electrolytic action, which forms a blanket or coating, and protects the metal from further action.

In the case of copper in steel, we should always take into account the fact that an oxide coating formed of iron and copper oxides is probably more resistant to further corrosion or to solution than plain simple oxide of iron.

Messrs. Thompson and Atchison show in their paper that magnetite anodes containing 5 percent of copper oxide are less corroded that pure magnetite, so that the presence of the copper oxide with the iron oxide increases the resistance to solution. This may probably account for the resulting resistance to corrosion, provided the coating of oxide is continuous.

F. A. LIDBURY[11]: In spite of the fact that there has been probably more work done on this particular set of studies or set of subjects than on any one of similar size, frequency or importance, it is less understood and less well explained. The reason for this appears to lie in the mental attitude of 99 percent of the workers who approach this subject. They seem to want to class all the so-called corrosive actions, whether those due to the exposure to air, or to the action of acids or salts in solution, or to direct electrolytic action, not as separate instances of chemical phenomena, but as all belonging to one set of phenomena; in other words, as one phenomenon requiring a single explanation. Instead of that, corrosion should be regarded as a subject of study according to the individual aspect of each set of conditions.

[10] Professor of Metallurgy, Lehigh University.

[11] Works Manager, Oldbury Electrochemical Co., Niagara Falls, N. Y.

E. A. RICHARDSON (*Communicated*): We do not see how silicon in cast iron can protect the iron (as suggested by Mr. Carl Hering) in the way that zinc protects iron in a heterogeneous mixture, even though it be electro-positive to iron. When one metal protects another by being electro-positive to it, it does so at its own expense. Since silicon exists in cast iron as a solid solution, the mixture is homogeneous as far as silicon is concerned.

Mr. C. F. Burgess has evidently confused our paper with the electrolysis of cast-iron pipe due to stray currents. We have been unable to find that any considerable work has been done on the corrosion of cast iron as stated by Mr. Burgess.

We are not ready to admit that the "barrier" theory advanced by Prof. Howe explains the corrosion of cast iron. We expect to be able to throw some light upon this theory at some future date.

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 4, 1917, President FitzGerald in the Chair.

ACID RESISTING PROPERTIES OF SOME IRON-SILICON ALLOYS.

By O. L. Kowalke.

[*Abstract.*]

Eighteen low-carbon iron-silicon alloys, containing 1.2 to 19.8 percent of silicon, were immersed from periods of 51 hours to 29 days in ten percent solutions of sulphuric, hydrochloric, nitric, acetic and citric acids, and the losses determined. With a few irregularities the resistance to acid attack was a minimum at 1.2 to 3.3 percent silicon, and a maximum at 16 to 18 percent. The latter alloys are very hard and brittle. Attempts are being made to find an addition element which will decrease these undesirable qualities while not impairing the resistance to acids.

Various acid-resisting alloys of commercial importance have been produced within recent years, and among these the iron-silicon alloys seem to give satisfactory service in many operations. There seems to be, however, but little published information on the acid-resisting properties of the iron-silicon alloys, and it was the purpose of this investigation to determine the resistance to several common acids. This paper is offered as a progress report with the hope that suggestions may be made which will be of assistance in the subsequent tests.

The assistance of Mr. Stanton Umbreit in obtaining these data is hereby gratefully acknowledged.

W. Guertler and G. Tamman[1] worked out the equilibrium diagram for these alloys. The curve shows mixed crystals or a solid solution of Fe and FeSi between 0 and 20 percent silicon. At 20 and at 33.7 percent silicon there are two compounds, Fe_2Si and FeSi respectively, which combine to form a eutectic at about 21.4 percent silicon. The compound FeSi and free silicon form a eutectic at 60.6 percent silicon, which corresponds to the formula $FeSi_3$. The melting point of Fe_2Si is about 1,250° C. and that of FeSi about 1,443° C. The alloys made for this investi-

[1] Zeit. Anorg. Chem., 47, 163-179.

gation lay in the region of mixed crystals, and did not contain over 20 percent silicon.

Preparation of the Alloys.

The alloys were made from electrolytic iron and ferro-silicon which analyzed 49.5 percent silicon; no test was made for carbon. Acheson graphite crucibles lined with magnesium oxide were used to melt the alloys. Each charge was made up to a total weight of 200 grams and the amount of ferro-silicon for each alloy was computed from the amount of silicon to be added. The charges were melted in the covered crucibles in a granular carbon resistor furnace.

The mold for casting the alloys was made from Acheson graphite. Recesses 4 x 1¼ x $\frac{1}{16}$ in. (10.15 x 3.2 x 0.15 cm.) were cut into a slab of graphite and a cover clamped onto the slab; pouring cups were also cut at the mouths of the recesses. This provided means for making a specimen about 3 x 1¼ x $\frac{1}{16}$ in. (7.62 x 3.2 x 0.15 cm.).

The alloys were not stirred while in the furnace, but as the crucibles containing the fluid alloys were removed from the furnace they were given a gyratory motion so as to mix the molten charge thoroughly. The melted alloys were then poured from the crucibles into the molds. As soon as the alloys solidified in the mold, the cover clamped over the recess was removed, and the alloy taken out.

Since the alloys cooled very rapidly upon being poured into the mold, there was undoubtedly a negligible amount of carbon absorbed, but no chemical analyses were made to prove this point.

The alloys of low silicon content made good soft castings. Above 3.5 percent silicon the alloys were brittle. In alloys of 7.5 percent silicon and above there were such severe strains developed on casting that they would frequently break into small pieces in the mold. Some alloys with more than 11 percent silicon would fly apart with great violence. Two castings with 16 percent and 17 percent silicon broke in the acid during corrosion tests the second week after casting the same.

Acid Corrosion Tests.

The acids used were ten percent solutions by weight of sulphuric, hydrochloric, nitric, acetic, and citric acids, made to this

strength by using a hydrometer. The temperatures of the acids when made and when used in the tests were between 20° and 25° C.

Owing to the great brittleness of the alloys, the specimens thereof used for the tests were very irregular in shape. The faces and edges of the specimens were therefore ground to fairly smooth surfaces.

The specimens were placed on edge in hard-rubber racks, which held the specimens rigidly and prevented them from touching one another. From thirteen to eighteen specimens could be placed on the various sized racks. The specimens on the racks were then placed in crystallizing dishes about 2 inches (5.1 cm.) deep and covered with the acid. A glass cover was placed over the dish to prevent evaporation.

From time to time the specimens were removed from the acid to be weighed. They were first washed in distilled water, then rinsed in denatured alcohol, and dried quickly in a current of hot air, after which they were weighed on an analytical balance.

Results.

The results of these tests are shown in Tables I to V. The percent loss is cumulative.

Sulphuric Acid: Tests given in Table I show that the loss is greatest at about 3.7 percent silicon, then the resistance increases to a maximum with a silicon content of 16 percent. Beyond this content of silicon the resistance seems to decrease.

Hydrochloric Acid: Tests given in Table II show that the loss is greatest at about 3.7 percent silicon, and least at about 18 percent silicon. Beyond this content of silicon there is a decrease in the resistance.

Nitric Acid: The loss diminishes quite steadily until the silicon content reaches 16 percent, after which it increased. The results are given in Table III.

Acetic Acid: The loss as shown in Table IV increases up to a content of silicon of about 5 percent, beyond this point it decreases steadily to 16 percent silicon, beyond which it again increases.

Citric Acid: From Table V it is seen that the corrosion increases up to a content of 3.3 percent silicon, beyond which it gradually decreases to the point where the silicon is 17 percent.

Table I: Loss in 10 Percent Sulphuric Acid.

Cumulative Loss, Percent.

Composition Percent Si	Area sq. cm.	51 hrs.	75 hrs.	141 hrs.	15 days	22 days	29 days
1.2	14.6	0.99	3.7	9.4	100	....	....
1.7	12.8	3.2	7.8	11.8	46.5	59.1	100
2.5	14.7	1.6	4.1	6.5	31.9	39.2	65.3
3.3	21.9	64.9	87.5	92.8	....	....	....
3.7	11.0	51.3	66.8	100.0	....	....	....
4.9	12.7	5.3	11.2	18.0	....	....	....
6.2	11.6	11.6	27.7	38.9	....	....	....
6.6	13.0	13.8	23.9	30.2	....	....	....
7.4	11.5	31.0	48.9	62.0	....	....	....
8.7	14.1	15.0	37.9	40.6	....	....	....
9.9	12.7	10.7	19.8	23.1	....	....	....
11.1	13.0	5.0	8.8	13.1	34.3	42.5	73.1
12.4	9.2	1.2	2.1	2.4	4.4	4.6	14.2
13.6	16.6	0.2	0.6	0.9	1.9	2.0	3.4
14.8	18.0	0.03	0.05	0.05	0.05	0.05	0.05
16.1	10.2	0.03	0.04	0.04	0.04	0.04	0.04
17.3	11.9	0.03	0.03	0.03	0.03	0.03	0.03
19.8	9.6	0.13	0.2	0.25	0.5	0.6	0.7

Table II: Loss in 10 Percent Hydrochloric Acid.

Cumulative Loss, Percent.

Composition Percent Si	Area sq. cm.	7 days	16 days	21 days	28 days
1.2	12.7	12.8	....	....	....
1.7	11.2	2.4	7.9	10.9	14.5
2.5	8.4	2.4	10.0	15.7	20.4
3.3	11.8	9.71	38.7	60.8	74.5
4.9	11.4	2.3	8.6	10.0	14.0
6.2	16.1	3.5	9.7	15.5	21.2
6.6	18.3	5.8	14.7	20.5	28.1
7.4	11.2	5.5	19.0	27.3	33.8
8.7	10.1	12.9	26.0	30.4	35.2
9.9	7.3	7.1	16.4	21.1	25.9
11.1	10.4	4.9	8.1	9.4	11.0
12.4	13.1	1.4	2.7	4.0	4.6
13.6	11.7	0.18	0.51	0.67	0.93
14.8	6.3	0.12	0.31	0.42	0.56
16.1	11.4	0.12	0.27	0.36	0.48
17.3	11.2	0.31	0.40	0.41	0.40
18.5	8.9	0.03	0.03	0.04	0.04
19.8	10.8	0.1	0.28	0.28	0.52

TABLE III: LOSS IN 10 PERCENT NITRIC ACID.

Cumulative Loss, Percent.

Composition Percent Si	Area sq. cm.	115 hrs.	166 hrs.	14 days
1.2	12.7	21.5	53.8	60.3
1.6	11.2	20.9	55.0	60.9
2.5	8.4	20.8	48.0	53.5
3.3	11.8	13.3	21.6	22.1
4.9	11.4	12.3	18.8	19.5
6.2	16.1	11.6	15.6	16.2
6.6	18.3	10.7	13.1	13.5
7.4	11.2	8.9	11.1	11.4
8.7	10.1	7.4	9.7	10.7
9.9	7.3	5.9	8.7	8.9
11.1	10.4	2.4	3.5	3.6
12.4	13.1	2.3	4.6	4.6
13.6	11.7	0.05	0.1	0.1
14.8	6.3	0.013	0.02	0.02
16.1	11.4	0.006	0.003	0.0015
17.3	11.2	0.006	0.007	0.007
18.5	8.9	0.037	0.044	0.046
19.8	13.8	0.01	0.01	0.01

TABLE IV: LOSS IN 10 PERCENT ACETIC ACID.

Cumulative Loss, Percent.

Composition Percent Si	Area sq. cm.	7 days	14 days	20 days	27 days
1.2	10.6	0.5	2.9	4.4	6.3
1.6	7.3	0.5	1.0	1.4	2.2
2.5	7.5	0.5	1.0	1.4	1.8
3.3	6.9	1.3	3.6	5.8	9.8
4.9	9.0	1.4	3.7	5.5	8.10
6.2	13.5	0.4	0.9	1.3	1.9
6.6	10.9	0.3	0.9	1.5	2.2
7.4	10.0	0.26	0.7	1.0	1.8
8.7	12.0	0.2	0.5	0.8	1.6
9.9	6.5	0.2	0.4	0.5	0.8
11.1	10.4	0.1	0.6	0.7	1.0
12.4	10.4	0.1	0.24	0.3	0.4
13.6	5.8	0.08	0.2	0.3	0.3
14.8	8.1	0.03	0.03	0.03	0.03
16.1	7.0	0.006	0.008	0.01	0.013
17.3	10.4	0.006	0.008	0.009	0.009
18.5	8.3	0.014	0.014	0.015	0.016
19.8	8.5	0.07	0.08	0.08	0.08

TABLE V: LOSS IN 10 PERCENT CITRIC ACID.

Cumulative Loss, Percent.

Composition Percent Si	Area sq. cm.	7 days	14 days	21 days
1.2	13.9	5.3	16.3	20.0
1.7	11.9	10.0	19.3	21.0
2.5	12.3	6.8	14.9	16.9
3.3	11.6	54.6	95.1	95.6
6.2	9.5	4.6	9.5	9.8
7.4	7.8	3.4	7.6	....
8.7	13.6	2.8	7.4	....
11.1	9.1	2.5	4.2	4.4
12.4	10.6	1.8	2.8	3.1
13.6	17.0	0.4	0.4	0.4
14.8	8.9	0.07	0.07	....
16.1	8.1	0.04	0.04	0.5
17.3	12.8	0.006	0.009	0.009

Conclusions.

Silicon-iron alloys of about 3 to 5 percent silicon are attacked very readily by sulphuric, hydrochloric, acetic, and citric acids. These alloys are not excessively brittle.

Silicon-iron alloys of about 16 to 18 percent are exceedingly resistant to action of sulphuric, hydrochloric, nitric, acetic, and citric acids. These alloys are so brittle that they must be ground; they can not be machined.

A solid solution of FeSi in iron near 20 percent silicon is resistant to mineral acids.

Search is in progress for a third metal which can be added to the iron-silicon alloys to improve their strength and still retain the resistance to the action of acids.

Chemical Engineering Laboratories,
University of Wisconsin.

DISCUSSION.

O. P. WATTS[1]: This paper was prompted by the commercial use of acid-resisting irons, with which many of you are familiar. This was an attempt to determine the action of some of the com-

[1] Asst. Professor of Applied Electrochemistry, University of Wisconsin.

mon acids upon iron alloyed with silicon, through the range in which these various commercial alloys are used.

C. F. BURGESS[2]: As far as I know, the manufacturers of these irons are not guaranteeing them as to their durability against these acids, especially hydrochloric acid. It seems to me that these tests, while interesting, are made under certain limitations, the conclusions of which cannot be accepted without reservation; that is, the temperatures are comparatively low, and there is no agitation. It is my impression that where you have boiling solutions and agitation, that you still have trouble when handling hydrochloric acid. I am wondering whether we may not have some statement from the producers of these irons along that line.

O. P. WATTS: While I agree with Prof. Burgess' statement that the matter of temperature is highly important, and that although these alloys will stand these acids at ordinary temperatures they might very well fail at higher temperatures, it seems to me the other point emphasized, that of circulation, is not particularly important. Where there is no chemical action the circulation, so it seems to me, can have no effect. Where there is chemical action, circulation is highly important. As far as the effect of circulation is concerned in these tests, at room temperature, it seems to me it is unimportant.

J. W. RICHARDS[3]: I believe that the copper depositing plant at Chuquicamata, Chile, in using duriron for anodes, had some trouble through the action of the sulphuric acid. They used up one pound of duriron for every five pounds of copper deposited.

Prof. Kowalke sent me specimens of his alloys recently, with which we intend to experiment to see how resistant they are as anodes in sulphuric acid solution.

W. C. BROOKS[4]: In commercial work experience has shown that the limitation of the alloy is not particularly in its resistance to chemical action, but to mechanical stresses.

If we could get a silicon-iron alloy with greater tensile strength or greater elasticity than some of the alloys produced at present, it would be much more useful.

[2] C. F. Burgess Laboratories, Madison, Wis.
[3] Professor of Metallurgy, Lehigh University.
[4] Chemical Engineer, National Carbon Co., Cleveland.

If these alloys were entirely resistant to sulphuric acid, so that we could with safety store a tank of acid, and know that it would dissolve practically no iron, it would be very important.

J. W. RICHARDS: In using the alloy as an anode these mechanical properties would be of only slight importance, but they are especially valuable for chemical apparatus. When they are used as anodes they simply hang on a hook, and have to resist very little mechanical stress.

W. C. BROOKS: I had particularly in mind the use of the material for pipes, plugs, cocks, etc.

W. R. MOTT[5]: These alloys, we know, are being used to a very large extent in nitric acid plants and other chemical works. I understand that in the present war it would have been impossible for Great Britain to have gotten along as well if it had not been for the application of the iron-silicon alloys, which are now used in the production of nitric acid on a scale never before practiced.

[5] Research Laboratory, National Carbon Co., Cleveland.

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, in Detroit, May 5, 1917, President FitzGerald in the Chair.

THE PRODUCTION AND PROPERTIES OF MAGNETITE ELECTRODES.[1]

By M. De Kay Thompson and T. C. Atchison.

[*Abstract.*]

1. A convenient method of making magnetite electrodes is described.

2. The toughness of anodes is shown to be greatly increased by the addition of copper oxide. The toughness increases linearly with the amount of oxide added.

3. The resistance to corrosion of the 5 percent copper oxide mixture when used as anode in a 10 percent sulphuric acid solution is greater than that of pure magnetite.

Magnetite electrodes were until recently extensively used at Chuquicamata, Chile, as anodes in the electrolysis of acid copper sulphate solutions. Chemically, they withstand the oxidizing effect of the current better than any other substance, but they have been practically given up on account of their extreme brittleness. "Duriron" has taken their place.

The object of the following work was to see whether the chief fault in these electrodes, their brittleness, could not be improved. A rumor had reached us that this could be done by the addition of a small amount of copper oxide to the magnetite, though we were never able to trace it to its source. The plan was to try the addition of this and other oxides and also to vary the heat treatment and measure the toughness of the resulting electrodes. On account of lack of time we were able to carry out only a part of this work.

[1] We wish to express our thanks to Professors H. W. Hayward and C. E. Locke and to Messrs. Freeman Clarkson and George Sutherland, for assistance and advice in connection with this work.

These electrodes can doubtless be cast from fused magnetite, but this is difficult when working with small quantities. The following method was found very easy to carry out and to give a very good product:

A 3.8 centimeter hole was drilled to a depth of 16.5 centimeters in a graphite rod 5.1 centimeters in diameter and 30 centimeters long. The whole electrode was held in a vertical position by firebricks with a copper holder at the bottom where electric connection was made. The other electrode consisted of an electric light carbon, 1.3 centimeters in diameter and 30 centimeters long. This was held by an iron stand mounted on two iron pipes as rollers so that it could be easily moved. In series with this furnace was a carbon plate rheostat, an ammeter, and the secondary of a transformer which supplied the heating current. The voltage measured at the transformer terminals was 60 and the current was about 200 amperes. The electric-light carbon was then lowered into the boring in the graphite until its end touched the bottom, an arc was struck and ground magnetite was fed in. This fused in the arc very rapidly and by watching the process through dark glasses it was easy to see when to add more magnetite. The boring was thus filled right up to the top and the electric light carbon was withdrawn gradually during the process. The first anodes were made without any attempt at annealing. When the upper end was nearly at the freezing point, there was always an evolution of some gas, causing a blow hole at that end. There were also occasional blow holes in other parts of the anode. There must have been some reduction to iron or to a lower oxide of iron, but it was so small in amount that it was not apparent. The fusion required about 30 minutes. After cooling, the anode was drawn out of the graphite tube. If it did not come easily a centimeter of the end of the tube was sawed off, so that the anode could be taken hold of, and so could easily be pulled out.

Attempts were also made to make anodes by passing an alternating current through the graphite tube and heat this to a temperature sufficiently high to melt the magnetite contained in it. There were evidences of reduction of magnetite to iron, however, and so this method was given up.

The method employed to test the brittleness of the anodes consisted in supporting them by two knife edges at the ends and

applying a load at the center, gradually increasing it until the specimen broke. This load is a measure of the toughness or brittleness of the material. The greater the length and the smaller the diameter of the rod tested, the more reliable is the result. Accordingly an attempt was made to make anodes only 2.5 centimeters in diameter. They broke so easily when handled that we returned to the original 3.9 centimeter diameter, but increased the length to from 24.1 to 26.6 centimeters. Allowing for an air hole and consequent weakness at the end, this length admitted testing with a 17.8 centimeter span. After some preliminary trials with a larger machine and the use of lead shot in a tin pail as load, a small Riehle testing machine, capable of measuring up to 9,000 kilograms, was found satisfactory when the load was applied very slowly by moving the belt by hand. The loads at which the specimens broke varied from 9 to 159 kilograms. Even though the measurement of these small loads may not have been very accurate, it is thought to be well within the precision of other experimental factors, especially the variation in brittleness due to the varying rate of cooling and the lack of uniformity in structure.

It was decided in this work to concentrate our attention to one oxide, and copper oxide was chosen. Specimens weighing from 1200 to 1300 grams, 3.8 centimeters in diameter, and 25.4 centimeters long were made from 99 percent magnetite[2], and varying amounts of copper oxide. The loads at the breaking point when applied at the center of a 17.8 centimeter span were measured and taken as a comparative test of their brittleness. The results are given in Table I and Fig. 1.

TABLE I.

Percent Copper Oxide	Load at Breaking Point. Kilograms				
	Single Observations				Average
0	11.3	17.3	20.4	27.2	19
1	18.2	26.3			22
2	18.2	43.1	50	46.8	39
5	36.3	42.2	47.6	76.2	50
10	52.2	58.1	59		56
20	104	130			117

[2] Obtained from Witherby, Sherman & Company, Fort Henry, New York.

While these observations show great variations due to accidental causes, in the average values these are more or less eliminated, and there is an unmistakable decrease in the brittleness with increasing amounts of copper oxide.

The effect of annealing was next tested. The graphite tube in which the electrode was made was placed in a vessel 25 centimeters in diameter and packed with asbestos. Three specimens of five percent copper oxide were made. The time required for cooling was about eight hours. They were tested exactly as in Table I and gave 105, 151, and 102 kilograms, average 119 kilograms, as the breaking load, or an increase of over 100 percent

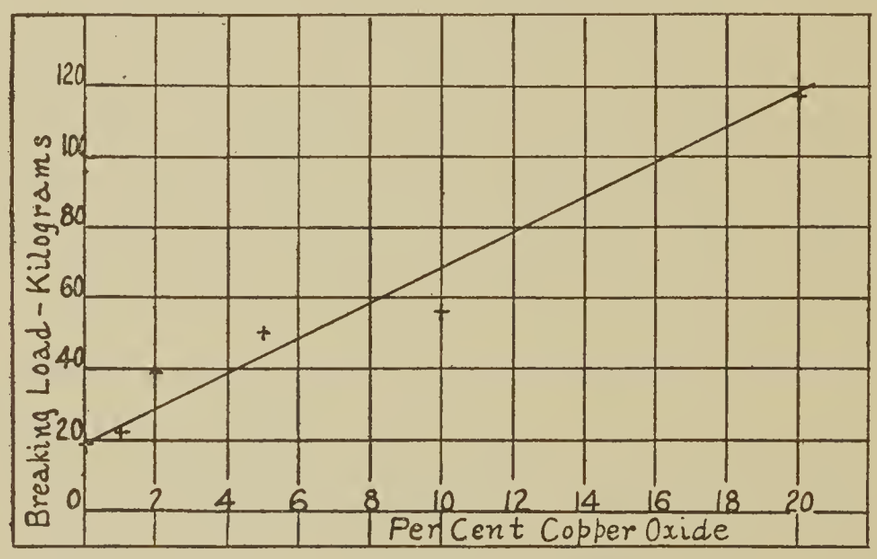

FIG. 1.

in the strength over those of the same composition which were cooled quickly. From external appearances they would have been considered to be of little value, for they were pitted with holes where the gas had escaped and the surface was rough. The cross section of the break was of a dull iron color in place of the usual crystalline structure.

The next experiments were for the purpose of testing the copper oxide-magnetite mixtures as to their behavior when used as anodes. Three specimens of pure magnetite and three containing 5 percent of copper oxide were placed in 10 percent sulphuric acid and used as anodes, with strips of copper as cathodes. Each anode dipped 10.2 centimeters into the acid in a separate vessel. As the water was decreased by electrolysis and boiling it was replaced automatically by a siphon which kept the solution at a

constant level and strength. All six cells were connected in series and 110 volts direct current were applied. The current was kept constant by a resistance in series. The current was about 4 amperes and the electrolysis lasted for 100 hours. The anode current density was about 3 amperes per square decimeter. The anodes were weighed before and after the electrolysis and the decrease in weight showed the degree of corrosion. Table II gives the results.

TABLE II.

Pure Magnetite Anodes.

Weight, Grams		Loss in Weight
Before Electrolysis	After Electrolysis	
1244	1180	64
1201	1150	51
1200	1150	50

Average 55 grams.

Average loss per square decimeter per 1000 ampere hours, 103 grams.

	95 Percent Magnetite	5 Percent Copper Oxide
1188	1141	47
1225	1200	25
1259	1228	31

Average 34.3

Average loss per square decimeter per 1000 ampere hours, 64.5 grams.

There is evidently also an improvement in the degree of anodic resistance to corrosion when 5 percent copper oxide is added. The greater loss in the pure magnetite may be in part due to the greater heating of these anodes by the current, on account of their resistance being greater than that of the 5 percent copper oxide mixture.

Massachusetts Institute of Technology,
Cambridge, Mass.

DISCUSSION.

PRESIDENT F. A. J. FITZGERALD[1]: At the FitzGerald Laboratories we made several experiments on making magnetite electrodes of various kinds, and our chief difficulty was their brittleness. We did not make them in the same way as the authors describe in this paper, but fused them in a radiation arc furnace and cast them in molds. We had a great deal of trouble with cracking, and even when we succeeded in getting the electrode out of the mold it was very brittle, and unless handled with great care would break. We tried a lot of experiments on annealing. We found that while the electrodes were at a good red heat, say 700° C., if we put them in an annealing furnace, kept them at a temperature of 600° or 700° C. for two or three hours and then gradually cooled them down, we got a relatively tough electrode and were able to make some having dimensions of 300 x 150 x 12 mm., which were quite strong.

B. I. WHITING[2] (*Communicated*): Before the start of the European war no one on this side of the Atlantic had been able to make magnetite anodes anywhere approaching the qualities of the German made article. Besides, the patent covering their manufacture was held by a German concern which exported to this country all the magnetite anodes used on this continent.

The natural supply being cut off by the war, several firms were put in the position of having to find either a substitute material or a new method of making them. The Chile Exploration Company very evidently resorted to both methods. Several alloys of the "Duriron" and other types were tested out thoroughly. At the same time a single-phase furnace with a single-top electrode was purchased and the services of an electro-metallurgist, well experienced in the development of electrochemical processes, were obtained. An anode was produced which in several respects even bettered the German product. The results were so satisfactory, indeed, that the furnace was dismantled, and, another one of four times the capacity of the smaller erected at another plant more suited for the commercial manufacture and shipment of the

[1] FitzGerald Laboratories, Niagara Falls, N. Y.

[2] Engineer, C. W. Leavitt Co., Agents for Girod Furnace, New York City.

anodes. The services of the electro-metallurgist were, however, in the meantime, dispensed with, and this may account for the statement in the paper that magnetite anodes have been practically given up on account of their extreme brittleness. I very much doubted the ability of the company to obtain at the new location and without the services of the aforementioned engineer the results obtained under his supervision, for these certainly justified the erection of a large plant for the manufacture of the anodes. Now, although the fact that the services of the same electro-metallurgical engineer are no longer obtainable may have no bearing on the matter, the company is carrying on experiments in the laboratories of one of our largest technical institutions. Another smelting and mining company has recently recognized the commercial value of such a procedure and is doing similar work at the Massachusetts Institute of Technology.

It is deeply to be regretted, however, that in neither case is it likely that others than the two companies concerned will profit through the purchased use of the facilities provided by the institutions of learning. Such arrangements should not exist unless it is provided that the results be published for the good of all.

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 5, 1917, President FitzGerald in the Chair.

THE ELECTROLYTIC BEHAVIOR OF TUNGSTEN.

WALTER E. KOERNER.

ABSTRACT.

The single potentials of tungsten in normal solutions of acids, alkalies, and neutral salts were calculated from E.M.F. measurements, and the results discussed.

The occurrence of tungsten as cation or anion, in different solutions, was investigated.

The passivity of tungsten in various solutions and under various conditions was studied.

The electrochemical equivalent was experimentally determined.

The use of tungsten in battery and storage cells was experimented with. The tungsten storage cell is particularly interesting.

PAPER.

The electrolytic behavior of tungsten has not been extensively investigated. Almost all of the earlier investigators have worked on the electrolytic deposition of metallic tungsten, their object being probably to produce tungsten in a tangible form by a relatively simple method.

The first researches upon the electrolytic reduction of tungsten were made from solutions of fused baths of tungstates. Zettnow,[1] in an article published in 1867, describes a black amorphous powder of metallic tungsten which he obtained, along with sodium bronze, by the electrolysis of molten sodium tungstates. Hallopeau[2] obtained by the electrolysis of molten lithium paratungstate, with platinum electrodes, crystals of metallic tungsten. Stavenhagen,[3] however, under the same conditions, obtained no metallic tungsten, but only lithium tungsten bronze. Scheibler[4] and Knorre[5] describe in their papers a large number of tungsten bronzes which they obtained by the electrolysis of molten tungstates.

Martin[6] obtained impure metallic tungsten by the electrolysis of tungstic acid dissolved in molten cryolite, analogous to the method of preparing metallic aluminium. The electrolysis of molten baths of halogen or oxyhalogen compounds of tungsten is not feasible, as these compounds are not very conductive.

Little is known about the electrolysis of aqueous and non-aqueous solutions of tungstates. Smith[7] observed that no effect is produced by the electrolysis of neutral solutions of tungstates, but that in acid solutions a blue color and a blue precipitate (presumably W_2O_5) is produced. The blue compound changes to brown as the current is allowed to run for some time. When the compound is exposed to the air after electrolysis, the brown changes back to blue.

The author does not agree entirely with Smith. I not only obtained the blue and brown compounds described by Smith, by the electrolysis of sodium tungstate acidified with H_2SO_4, but I also obtained a blue solution and a blue precipitate which turned to brown by the electrolysis of sodium tungstate in a neutral solution. The conditions, however, were somewhat different. Smith used platinum electrodes, while the author used tungsten electrodes.

Leiser[8] electrolyzed an acid solution of sodium tungstate between a nickel anode and a platinum cathode, and obtained a blue precipitate which when analyzed was found to be W_4O_{11}. With a lead cathode he obtained a brown deposit which probably was WO_2.

Rosenheim[9] electrolyzed a solution of H_2WO_4 in an alcoholic solution of HCl (gas). H_2WO_4 dissolved in this solution to the extent of 9.8 percent H_2WO_4. He used graphite as anode material. With a platinum cathode the reduction proceeded only as far as pentavalent tungsten (W^{v}). With mercury or cadmium cathodes, the reduction varied with the current density, while with zinc cathodes, the reduction proceeds to tetravalent tungsten (W^{IV}). Rosenheim obtained a series of oxides of tungsten varying from five to two. He obtained no metallic tungsten.

Up to that date, 1909, no satisfactory method had been developed for the electrolyte deposition of tungsten and no metallic tungsten had been obtained by electrolysis.

In June, 1910, a patent[10] was issued in Germany for the elec-

trolytic deposition of metallic tungsten from an aqueous or organic solution of pertungstic acid, H_4WO_6, or one of its salts.

In the same month of the same year, a second patent[11] was issued to the Wolfram-Lampen A.G. for the electrolytic deposition of tungsten from organic solution of WCl_6.

Fischer[12] tried to deposit metallic tungsten from solutions of WCl_6 in absolute ethyl alcohol saturated with HCl (gas) and from solutions of WCl_6 in glycerine. With the latter the concentration of the dissolved WCl_6 was too small for practical observations. Fischer used carbon as anode and platinum as cathode in his work. With a low concentration of WCl_3 (3 gm./150 c.c. of alcohol) he obtained a green solution, the green color being due to a reduction to pentavalent tungsten. He[13] found this green color to be due to a triethoxyl substitution product of tungsten pentachloride, $WCl_2\ (OC_2H_5)_3$.

With a higher concentration (22 grams of WCl_6 per 120 c.c. of alcohol) he obtained, on the cathode, a black precipitate which could not be strictly called tungsten metal. He decided that it was WO.

Fischer tried also to obtain tungsten by the method described by other German patents,[14] but without success. He obtained by the electrolysis of pertungstic acid, a blue-black precipitate which when analyzed showed 92.33 percent tungsten. This corresponds to WO.

It seems, in going over the literature, that although some of the earlier investigators thought that they had produced metallic tungsten by electrolysis, in nearly every case the precipitate obtained was some tungsten compound, principally WO and perhaps a lower oxide. Fischer tried to verify the claims made by the German patents, but he obtained no pure metal.

The work on the electrolytic behavior of tungsten, which the author here presents in a preliminary report, was divided into four subheads.

I. *Single potentials (E.P.) of tungsten:*

A. E.P. of tungsten in various electrolytes.

B. E.P. of tungsten in saturated solutions of tungsten hydroxide in various electrolytes, bearing on the solubility of tungsten oxide.

II. *The anodic behavior of tungsten, and its passivity:*

A. In acids and in neutral salt solutions in water.

B. In acids and in neutral salt solutions in organic solvents.

C. In inorganic and organic alkalies with a bearing on the electrolytic recovery of tungsten.

III. *The use of tungsten in cells:*

A. The use of tungsten in a voltaic cell.

B. The use of tungsten in a standard cell.

C. The use of tungsten in a storage cell.

IV. *Electrodeposition of tungsten:*

The author has reserved all observations made on the electrolytic deposition of tungsten for future publication.

I. SINGLE POTENTIALS OF TUNGSTEN.

The single potential measurements were made in order to obtain some light on the relative solubility of metallic tungsten in solutions of various electrolytes.

Insoluble electrodes would give single potentials of the positive and negative ions in solution. In a 1/1 n. NaOH solution we should get, if the anode were insoluble, the value of the oxygen electrode, 1.47 volts, hydrogen equal to zero (H = O). The single potential for tungsten in 1/1 n. NaOH solution is —0.316 volt (H = O) a value very much smaller than the oxygen potential. It follows, then, that the tungsten anode goes into solution in NaOH and ionizes. The rate of solution varies with the solvent used.

Three half cells were used as auxiliary electrodes in measuring the single potentials. The first, the normal KCl-calomel half cell was used with acid and salt solutions. The second, a half cell made from Hg, red HgO and 1/1 n. NaOH, was used with alkali solutions. A third, a half cell made from Ag, Ag_2O and 1/1 n. NaOH, was used as a check on the other two cells.

The n. KCl-calomel electrode was made according to standard specifications.[16] The single potential of this electrode was taken as +0.56 volt. The potential of the second cell, made with the same construction as the first, but having HgO substituted for

HgCl, and n. NaOH substituted for KCl, was taken as +0.445 volt.[17] The third cell, made from Ag, Ag_2O and n. NaOH, was taken as +0.655 volt.[18] The cells were checked up against each other and found to agree within amounts not greater than those allowed for experimental error.

In the combination,

$$Hg \mid HgCl \mid KCl \,||\, NaOH \mid HgO \mid Hg$$

the E.M.F. obtained was 0.1588 volt with the mercury in the calomel positive. If the single potential of the calomel electrode is +0.56 volt and that of the mercury oxide electrode is +0.445 volt, the E.M.F. produced by the combination, neglecting the liquid potential KCl | NaOH, should be +0.115 volt. Since we get an E.M.F. of 0.1588 volt we conclude that the liquid potential KCl | NaOH is +0.0438 volt.

Similarly with the combination,

$$Ag \mid Ag_2O \mid NaOH \,||\, KCl \mid HgCl \mid Hg$$

(the silver being positive) we get an E.M.F. of +0.0488 volt. The value of the liquid potential KCl | NaOH is calculated to be in this case +0.0462 volt.

$$+0.655 + x + (-0.56) = 0.0488$$
$$x = -0.0462$$
$$x = NaOH \mid KCl = -0.0462$$
$$\text{then } -x = KCl \mid NaOH = +0.0462$$

Finally in the combination,

$$Ag \mid Ag_2O \mid NaOH \,||\, NaOH \mid HgO \mid Hg$$

with silver positive, the E.M.F. obtained was 0.209 volt. This checks up with 0.210 volt = +0.655 + (—0.445).

The tungsten electrodes used in these measurements were 75 mm. long and 3.2 mm. in diameter. They were made from a high-grade tungstic acid which was reduced to tungsten metal by hydrogen. The metal powder was pressed into a rod at a high pressure and melted electrically in hydrogen. After cooling in the same gas, the rod was hot-swaged to size, cut in half, and two electrodes of the same composition obtained.

Before making the choice of this form of tungsten metal, we made several single potential measurements with different kinds of so-called tungsten metal, made by different processes. It was found that the potential of these various metals in 1/1 n. NaOH varied within wide limits. A black finely divided metal powder had a single potential of —0.704 volt (H = O), while gray compact melted rod had a single potential (E.P.) of —0.316 volt (H = O). See following table.

Upon closer and further observations we concluded that the finely divided black metal contained a lower form of oxide, either as a mechanical mixture, or adsorbed to and covering the metal particles. The high E.P. in this case is not the W | NaOH potential but the E.P. of W_xO_y | NaOH. Tungsten oxides are more soluble in NaOH than tungsten, and have higher E.P.'s in NaOH than tungsten.

Following is a table showing the E.M.F.'s as measured with the Hg | HgO NaOH electrode, of various forms of tungsten metal. The E.P.'s are expressed in terms of calomel = O, calomel = +0.56 and Hydrogen = O.

TABLE I.

1.	2.	3.	4.	5.
Form of Metal	E. M. F.	E. P. Cal. = O	E. P. H = O	E. P. Cal. = + 0.56
Black powder	+ 0.872 V.	— 0.987 V.	— 0.704 V.	— 0.427 V.
Gray "	+ 0.776 "	— 0.891 "	— 0.608 "	— 0.331 "
At. Wt. "	+ 0.667 "	— 0.782 "	— 0.499 "	— 0.222 "
Rod No. 1	+ 0.573 "	— 0.688 "	— 0.405 "	— 0.128 "
" " 2	+ 0.561 "	— 0.676 "	— 0.393 "	— 0.116 "
" " 3	+ 0.494 "	— 0.609 "	— 0.326 "	— 0.049 "
At. Wt. Rod	+ 0.484 "	— 0.599 "	— 0.316 "	— 0.039 "

Column 2 in Table I gives the E.M.F. values as actually measured. They may also be taken as E.P.'s of NaOH | W when the value of the auxiliary electrode is taken as zero. The E.P.'s of W | NaOH would be the same values numerically but opposite in size.

It was suggested, at the International Congress of Berlin,[19] that in all cases the directly measured values be given and that the 1/1 n. KCl calomel or the Nernst hydrogen electrodes be employed as auxiliary electrodes and taken as zero. These direct measurements may be taken as the E.P.'s of the combinations referred to the calomel or hydrogen electrodes as zero. (Cal. = O) (H = O).

Since we used the HgO half cell (already described) as the auxiliary electrode, it is necessary to calculate to the calomel values. The relation of calomel to mercury oxide is,

$$\text{E.P.}_{\text{Cal.}} = \text{E.P.}_{\text{HgO}} + 0.115 \text{ volt.}$$

It follows that in order to change the HgO values to calomel values, it is only necessary to add 0.115 volt to the E.M.F. readings and change the signs to reduce these to W | NaOH. These E.P.'s are shown in column 3. (Cal. = O).

A relation also exists between the E.P. of the hydrogen electrode and that of the calomel electrode. This relation is expressed by

$$\text{E.P.}_{\text{H}} = \text{E.P.}_{\text{Cal.}} + 0.283 \text{ volt.}^{20}$$

Column 4 gives the E.P.'s of W | NaOH compared to H = O. Column 5 gives the values in terms of cal. = +0.56 volt.

The E.M.F.'s given in the above and the following tables were obtained by means of a Wolff potentiometer connected, with a standard Weston element, to a small storage cell to furnish current and a D'Arsonval galvanometer. After compensating the standard Weston element and the storage cell, the potentiometer was adjusted to zero swing on the galvanometer. The E.M.F. was read directly from the potentiometer.

The customary precautions were taken in connecting up the cells to prevent the different electrolytes from mixing. Glass U tubes 80 mm. long and 2 mm. bore, through which clean cotton cord was passed, served to connect one electrolyte with another. In some cases, a cup containing the same electrolyte as the one in which the tungsten was immersed, was interspersed between the latter and the cup containing the second electrolyte. This was to

further reduce the contamination of the first electrolyte with the second. Following are the results obtained with W in the various electrolytes used.

TABLE II. 1/1 N. ACIDS.

Measured with auxiliary electrode Hg | HgCl | KCl = +0.56 volt.

1.	2.	3.	4.	5.	6.	7.	8.
1/1 n. Acid	E.M.F. Volts	E.P. W | sol cal = +0.56 Volts	E.P. KCl | sol Volts	E.P. W | sol Corrected cal = +0.56 Volts	E.P. W | sol cal = O Volts	E.P. W | sol Corrected cal = O Volts	E.P. W | sol H = O Volts
H_2SO_4 ..	+0.060	+0.500	—0.030	+0.470	—0.060	—0.090	+0.193
HCl	—0.0028	+0.562	—0.029	+0.533	+0.0028	—0.027	+0.256
HNO_3 ..	—0.057	+0.617	—0.029	+0.588	+0.057	+0.028	+0.311

TABLE III*a*. 1/1 N. BASES.

Measured with auxiliary electrode Hg | HgO | NaOH = +0.445 volt.

1.	2.	3.	4.	5.	6.	7.
1/1 n. Base	E.M.F. Volts	E.P. W | sol HgO = +0.445 Volts	E.P. HgO | sol Volts	E.P. W | sol Corrected HgO = +0.445 Volts	E.P. W | sol cal = O Volts	E.P. W | sol H = O Volts
KOH	+0.481	—0.036	—0.002	—0.038	—0.598	—0.315
NaOH	+0.484	—0.039	0	—0.039	—0.599	—0.316
NH_4OH	+0.406	+0.039	——	+0.039	—0.521	—0.238
KCN	+0.715	—0.370	——	—0.370	—0.930	—0.647

TABLE III*b*. 1/1 N. BASES.

Measured with the auxiliary electrode Ag | Ag_2O | NaOH = +0.655 volt.

1.	2.	3.	4.	5.	6.	7.
1/1 n. Base	E.M.F. Volts	E.P. W | sol HgO = +0.445 Volts	E.P. HgO | sol Volts	E.P. W | sol Corrected HgO = +0.445 Volts	E.P. W | sol cal = O Volts	E.P. W | sol H = O Volts
KOH	+0.690	—0.035	—0.002	—0.037	—0.597	—0.314
NaOH	+0.694	—0.039	0	—0.039	—0.599	—0.316
NH_4OH	+0.615	+0.040	——	+0.040	—0.520	—0.237
KCN	1.034	—0.379	——	—0.379	—0.939	—0.656

Table III*c*. 1/1 n. Bases.

Measured with the auxiliary electrode Hg | HgCl | KCl = +0.56 volt.

1.	2.	3.	4.	5.	6.	7.
1/1 n. Base	E.M.F. Volts	E.P. W | sol cal = +0.56 Volts	E.P. KCl|NaOH Volts	E.P. W | sol Corrected cal = +0.56 Volts	E.P. W | sol cal = O Volts	E.P. W | sol H = O Volts
NaOH	+0.648	—0.088	—0.048	—0.040	—0.600	—0.317

Table IV. Halogen Salts 1/1 n.

Measured with the auxiliary electrode Hg | HgCl | KCl = +0.56 volt.

1.	2.	3.	4.	5.	6.	7.
Salt	E.M.F. Volts	E.P. W | sol cal = +0.56 Volts	E.P. KCl | sol Volts	E.P. W | sol Corrected cal = +0.56 Volts	E.P. W | sol cal = O Volts	E.P. W | sol H = O Volts
KF	+0.235	+0.325	—0.0037	+0.2213	+0.239	+0.522
KCl	+0.280	+0.280	0	+0.280	+0.280	+0.563
KBr	+0.306	+0.264	+0.0004	+0.264	+0.306	+0.589
KI	+0.450	+0.11	+0.0002	+0.11002	+0.450	+0.733

Table V. K Salts of Acids of Table II.

Measured with the auxiliary electrode Hg | HgCl | KCl = +0.56 volt.

1.	2.	3.	4.	5.	6.	7.
Salt	E.M.F. Volts	E.P. W | sol cal = +0.56 Volts	E.P. KCl | sol Volts	E.P. W | sol Corrected cal = +0.56 Volts	E.P. W | sol cal = O Volts	E.P. W | sol H = O Volts
K_2SO_4	+0.430	+0.130	—0.006	+0.124	+0.436	+0.719
KCl	+0.280	+0.280	0	+0.280	+0.280	+0.563
KNO_3	+0.017	+0.593	—0.0007	+0.543	+0.017	+0.300

In Table II, column 1 gives the 1/1 n. acid solutions in which the tungsten rod was immersed. Column 2 gives the E.M.F.'s measured with the calomel electrode as an auxiliary electrode. Column 3 shows the calculated E.P.'s of W | sol compared to

calomel = +0.56 volt disregarding liquid potential KCl | acid sol. Column 4 gives the E.P.'s KCl | acid sol. calculated from Planck's formula

$$\text{E.P.} = 1.99 \times 10^{-4}\ T \log \left(\frac{U_1 + V_2}{U_2 + V_1}\right)$$

Column 5 shows the E.P.'s W | sol. corrected for liquid potential KCl | acid sol. (calomel = +0.56 volt). Column 6 gives the E.P.'s for W | sol. compared to calomel = O not corrected for liquid potentials, while column 7 gives the E.P.'s for W | sol. (cal = O) corrected for E.P.'s KCl | acid sol. Column 8 gives the E.P.'s for W | sol. compared to H = O.

Table III gives the same results for bases as Table II gives for acid. In this case the auxiliary electrode Hg | HgO | NaOH = +0.445 volt was used. Column 5 gives the E.P. W | sol. compared to HgO = +0.445 volt. These values are identical to E.P. W | sol., compared to cal. = +0.56 volt. From these figures the E.P. W | sol values compared to cal. = O are obtained and given in column 6. The E.P.'s W | sol. H = O are shown in column 7.

Tables III *b* and III *c* are practically the same except that in the former case we used the silver oxide electrode, while in the latter we used the calomel electrode. Table IV gives the results obtained with 1/1 n. solution of the halogen salts of K, and Table V the results obtained with K salts of the acids shown in Table II.

It is seen from Table II that the E.P. W | 1/1 n. acid sol. varies with the acid used, and that it is highest with HNO_3 and lowest with H_2SO_4. Tables III *a*, III *b*, and III *c* show that with KOH and NaOH the E.P.'s are practically the same, while with NH_4OH the E.P. is lower numerically and higher algebraically than those of NaOH or KOH. The E.P. of W | KCN is much higher numerically (and lower algebraically) than any of the others. Tables IV and V show the E.P. for W | sol. in the various salts.

The single potential of tungsten in 1/1 n. HNO_3 may be compared to the single potential of copper in 1/1 n. (ion concentration) $CuCl_2$ solution. The E.P. of Cu | $CuCl_2$ is +0.329 volt (H = O)[21] while that of As | $AsCl_3$ is +0.293 volt (H = O).

The single potential of W in the alkalies may be compared in the same way; that of W in KCN being higher than iron but lower than nickel; the single potential of W in NaOH, KOH and NH_4OH being higher than that of thallium but lower than that of tin. In like manner the single potentials of W in the halogen and other salts can be compared with the single potentials of other metals.

We have arranged a relative single potential table in order of increasing E.P. (algebraically), from the lowest algebraic value to the highest algebraic value. See Table VI. In column 2 are given the E.P.'s of W | sol. calculated from the measurements taken. Column 3 gives the E.P.'s for Fe, Ni, Tl, etc., taken from Le Blanc.

TABLE VI.

1.	2.	3.	4.
	E.P. W | sol H = O Volts	E.P. H = O Le Blanc Volts	
		—0.660	Fe
KCN	—0.647		
		—0.600	Ni
		—0.322	Tl
NaOH	—0.316		
KOH	—0.315		
NH_4OH	—0.238		
		—0.192	Sn
		—0.148	Pb
		0	H
H_2SO_4	+0.193		
HCl	+0.256		
		+0.293	As
KNO_3	+0.300		
HNO_3	+0.311		
		+0.329	Cu
		+0.466	Sb
KF	+0.522		
KCl	+0.563		
KBr	+0.589		
K_2SO_4	+0.719		
KI	+0.733		
		+0.750	Hg

It was not possible to determine the E.P. of tungsten in aqueous solutions of its salts, because the salts of tungsten, *e. g.*, the hexachloride and hexabromide are readily decomposed by water.

Fischer[22] and others have found that WCl_6 dissolves very readily in many organic solvents without decomposition, and that some of the solutions are quite conducting. Fischer chose, as a specific solvent, absolute ethyl alcohol, and measured the E.P. of W | WCl_6 in solutions of varying concentrations of WCl_6, using, as an auxiliary electrode, a calomel half cell, the electrolyte of which was a saturated solution of lithium chloride in alcohol. He found that a 0.102 n. molecular solution of WCl_6 produced, along with the auxiliary half cell, an E.M.F. of 0.465 volt, the tungsten being positive. From this value he calculated the E.P. of W | 1/1 n. (ionic) sol. WCl_6 to be 0.680* volt (H = O). He also calculated that the $E.P._{H_2O-C_2H_5OH}$ to be 0.071 volt. He assumes that $E.P._{W-WCl_6(C_2H_5OH)} - E.P._{H_2O-C_2H_5OH} - E.P._{W-WCl_6(H_2O)}$ and substituting the values obtained above he gets $E.P._{W-WCl_6(H_2O)} = 0.609$ volt (H = O), a hypothetical value. He decides that W lies between Sb and Hg in the electrochemical series given by Le Blanc.

Analogous to Fischer's experiments we thought it possible to find the E.P. of W in saturated solutions of $W(OH)_6$ in 1/1 n. HCl, H_2SO_4 and HNO_3 and from the E.P.'s obtained to calculate the E.P.'s in 1/1 n. (ionic) solution of $W(OH)_6$. The solutions of $W(OH)_6$ were prepared by electrolyzing the solvents between tungsten electrodes until a copious excess of yellow precipitate was obtained. The anode during electrolysis in each case went through a series of color changes from brown through blue to yellow, after which tungstic acid was precipitated from the solution. These color changes will be discussed later. We considered the solvents saturated with $W(OH)_6$ when the precipitate began to form. The reactions which take place at the anode during electrolysis produce a hydroxide of tungsten, which dissolves to saturation and ionizes. When the solvent is saturated with ions, the molecular $W(OH)_6$, being unstable, breaks down to H_2WO_4 and analogous compounds by the loss of water. The reactions expressing these changes being,

$$W(OH)_6 = WO(OH)_4 + H_2O$$
$$W(OH)_6 = WO_2(OH)_2 + 2H_2O$$
$$W(OH)_6 = WO_3 + 3H_2O$$

* Fischer has confused his signs in his calculations.

The end product, anhydrous WO_3, is probably never reached in this case.

Analogous reactions occur between ionic chlorine and tungsten. Tungsten hexachloride forms and dissolves. Being unstable in water, it immediately decomposes to $W(OH)_6$.

$$WCl_6 + 6H_2O = W(OH)_6 + 6HCl$$

$W(OH)_6$ dissolves to saturation and the excess breaks down to WO_3 in the same manner as in the above case. In case either Cl ions or OH ions are discharged at the anode, the end product will be the same. Analogous reactions occur in HNO_3 and H_2SO_4 solutions.

That W and Cl ions do unite to form WCl_6 has been shown by electrolyzing a saturated solution of HCl (gas) in absolute ethyl alcohol between tungsten electrodes which have been separated by a porous cup. The anode solution becomes colored yellow by the dissolved WCl_6 that has been formed.

Our E.M.F. measurements, Table IX, have shown that $W(OH)_6$ is not only soluble in 1/1 n. HCl, H_2SO_4 and HNO_3, but also that the $W(OH)_6$ is ionized to W ions and OH ions. It is dissolved as a true solution and not a colloidal solution, though some colloidal tungstic acid may be present in the solution. Unless the $W(OH)_6$ were ionized, no E.M.F. would have been obtained in the combination,

$$\begin{array}{l} W \mid W(OH)_6 \parallel HCl \mid W \\ W \mid HCl \quad\quad \parallel \quad\quad \mid \end{array} \qquad \text{(See Table IX.)}$$

We have assumed that the dissolved tungsten is present as a hydroxide, $W(OH)_6$ and that this hydroxide ionizes to W ions and OH ions in the same manner that $Pb(OH)_4$ ionizes to Pb ions and OH ions in the lead accumulator[23 and 24]. According to Dolezalak,[24] PbO_2 hydrolyzes to $Pb(OH)_4$ which ionizes to a tetravalent lead ion and four OH ions.

If $W(OH)_6$ is an amphoteric electrolyte,[25] the tungsten in solution must migrate as cations to the cathode in acid solution, and as anions to the anode in alkaline solution.[26]

From direct measurements, the combination

$$W \;\Big|\; \begin{matrix} H_2SO_4 \\ W(OH)_6 \end{matrix} \;\Big\|\; H_2SO_4 \;\Big|\; W$$

gave an E.M.F. of +0.117 volt with the tungsten in the $W(OH)_6$ as positive. This shows that the half cell $W^{W(OH)_6}_{H_2SO_4}$ is 0.117 volt more positive than the half cell in which there is no $W(OH)_6$ in solution. The combination is a concentration cell, the right-hand member being the more dilute with respect to $W(OH)_6$.

According to Nernst,[27] the dilute solution always presents the sign of the more rapidly moving ion. It is obvious that the mobility of the OH ion is much greater than that of the W ion. The more dilute solution will then be negative to the more concentrated with respect to $W(OH)_6$. The concentration of the H and the SO_4 ions are the same in both half cells.

If instead of having $W(OH)_6$ in solution, we had paratungstic acid, $H_6W_7O_{24}$, or ortho tungstic acid, H_2WO_4, we would have WO_4 ions and an increased number of H ions in the right-hand half cell (assuming H_2WO_4 dissolved). Since the H ion is more mobile than the WO_4 ion, the more dilute solution would then be positive. Experiment showed, however, that the more dilute solution is negative, taking the sign of the more mobile of the ions resulting from the dissociation of the $W(OH)_6$. Tungsten must then exist as the cation in solution, and the solution must contain $W(OH)_6$.

Following are the results of the experiment.

TABLE VII. 1/1 N. ACIDS NO $W(OH)_6$ DISSOLVED.

Measured with auxiliary electrode cal = +0.56 volt.

1.	2.	3.	4.	5.	6.	7.	8.
1/1 n. Acid	E.M.F. Volts	E.P. W | sol cal = +0.56 Volts	E.P. KCl | sol Volts	E.P. W | sol Corrected cal = +0.56 Volts	E.P. W | sol cal = O Volts	E.P. W | sol Corrected cal = O Volts	E.P. W | sol H = O Volts
H_2SO_4	+0.058	+0.502	—0.030	+0.472	—0.058	—0.088	+0.195
HCl ..	—0.006	+0.566	—0.029	+0.537	+0.006	—0.023	+0.260
HNO_3	—0.054	+0.614	—0.029	+0.585	+0.054	+0.025	+0.308

TABLE VIII. 1/1 N. ACIDS SAT. WITH $W(OH)_6$.

Measured with auxiliary cal. electrode = +0.56 volt.

1.	2.	3.	4.	5.	6.	7.	8.
1/1 n. Acid	E.M.F. Volts	E.P. W | sol cal = +0.56 Volts	E.P. KCl | sol Volts	E.P. W | sol Corrected cal = +0.56 Volts	E.P. W | sol cal = O Volts	E.P. W | sol Corrected cal = O Volts	E.P. W | sol H = O Volts
H_2SO_4	—0.06	+0.620	—0.030	+0.590	+0.06	+0.030	+0.313
HCl ..	+0.063	+0.623	—0.029	+0.594	+0.063	+0.034	+0.317
HNO_3	+0.063	+0.623	—0.029	+0.594	+0.063	+0.034	+0.317

TABLE IX. HALF CELL COMBINATIONS.

W | H_2SO_4, $W(OH)_6$ || H_2SO_4 | W	+0.117 Volt
W | HCl, $W(OH)_6$ || HCl | W	+0.057 Volt
W | HNO_3, $W(OH)_6$ || HNO_3 | W	+0.009 Volt

In Table VII the E.P.'s of W in 1/1 acid sol. are shown. Table VIII shows the E.P.'s of W in 1/1 n. acid solutions saturated with $W(OH)_6$.

Table IX shows the order of solubility of $W(OH)_6$ in the three acids. It is least soluble in HNO_3 and most soluble in H_2SO_4. In each of the three cases the E.M.F. is the result of the difference of concentrations in the two members of the cell. The concentrations of the $W(OH)_6$ in the right-hand members are very small. We determined the amount of $W(OH)_6$ that is dissolved in the three 1/1 n. acid solutions to saturation by evaporating a large volume of the solution to dryness, igniting and weighing as WO_3. We find

0.02281 gm. WO_3 = 0.02816 gm. $W(OH)_6$ per 1000 c.c. n/n H_2SO_4
0.01067 gm. WO_3 = 0.01315 gm. $W(OH)_6$ per 1000 c.c. n/n HCl
0.00025 gm. WO_3 = 0.00030 gm. $W(OH)_6$ per 1000 c.c. n/n HNO_3

If we try to calculate the concentration of the $W(OH)_6$ in solution by means of the modified Nernst formula

$$E.P. = \frac{0.058}{V} \log \left(\frac{C_1}{C_2}\right)$$

where C_1 and C_2 are the ionic concentrations, we run into difficulties.

We can not calculate the concentration of $W(OH)_6$ by conductivity measurements because the conductivity of the 1/1 n. acid solutions are so high and the concentration of the $W(OH)_6$ is so low, that the increase in conductivity due to $W(OH)_6$ would not be much greater than a value due to experimental error.

From the values of concentration found by evaporating to dryness, we can calculate the E.P. for W | 1/1 n. $W(OH)_6$.

$$E.\ P._n = E.\ P. - \frac{0.058}{V} \log c$$

This was found to be 0.336 volt in 1/1 n. H_2SO_4, 0.342 volt in 1/1 n. HCl, 0.358 volt in 1/1 n. HNO_3.

II. ANODIC BEHAVIOR OF TUNGSTEN IN ELECTROLYTES.

Le Blanc[28] studied the anodic behavior of tungsten in various electrolytes and found that in 1/1 n. solutions of H_2SO_4, HCl and HNO_3 the metal becomes passive. In KOH, NH_4OH, NaOH, however, he found that the metal stays active within wide ranges of current density. If, however, the current density reaches or exceeds a maximum in alkaline solutions, tungsten becomes passive. Interrupting the current for a short time destroys the passivity.

From experiments which we have made, we have noticed that when 1/1 n. solution of HCl, H_2SO_4, HNO_3, KF, KCl, KBr, KI, K_2SO_4, and KNO_3 are electrolyzed between tungsten electrodes separated by a porous cell, the anode always becomes coated with a series of films ranging in color from brown through purple, dark blues, light blues, greens, to yellow. The color changes are *independent* of the nature of the anions and cations in the solution used, but are *dependent* upon the current density and the time of electrolysis. With an initial current density of approximately 0.00025 amp. per square dm., the color changes of the film on the anode can be very easily followed. I use the term initial current density to denote the current at the start. As the electrolysis proceeds, the resistance of the film increases and the current flowing is decreased. The first flash of brown color is quite marked and the change from brown to purple is also quite

marked. The change to dark blue and to light blues is slower, and it is difficult to tell when the greens stop and the yellow begins. The change from green to yellow is gradual. These changes are a function of current density and time. Tables XI, XII, and XIII give comparative figures on three runs which we made with a 1/1 n. solution of KCl.

TABLE XI.

Time	Current Amperes	Back E.M.F. Volts	Color
0 sec.	0	0	Gray (tungsten)
2	0.0400	1.325	Brown
5	0	1.350	Purple-Brown
7	0	1.350	Purple
10	0	1.350	Dark Blue
12	0	1.375	Light Blue
20	0.0270	1.425	Green Blue
30	0.0225	1.460	Olive Green
60	0.0175	1.480	Yellow Green
80	0.0165	1.50	Yellow
100	0.0150	1.54	Yellow

TABLE XII.

Time	Current Amperes	Back E.M.F. Volts	Color
0 sec.	0	0	
2	0.065	1.0	Brown
5	0	1.1	Purple-Brown
7	0	1.1	Light Blue
10	0.035	1.15	Light Blue
15	0	1.225	Green Blue
20	0.028	1.25	Yellow-Green
30	0.025	1.325	Yellow

TABLE XIII.

Time	Current Amperes	Back E.M.F. Volts	Color
0 sec.	0	0	
2	0.085	0.93	Brown
5	0	1.10	Light Blue
7	0	1.10	Light Blue
10	0.045	1.20	Green Blue
15	0	1.25	Yellow
20	0.040	1.35	Yellow

If the initial current density be increased to 2 amp. per sq. dm., the anode assumes a yellow color almost immediately. The eye, not being quick enough to follow the color change from brown to yellow, sees only the yellow.

Rosenheim obtained a similar series of colored oxides, in reversed order, by the cathodic reduction of H_2WO_4. He started with yellow and ended with brown WO_2. Our results are analogous to his, in that we have the same series of colors formed electrolytically, but differ from his results in that we have anodic oxidation and Rosenheim had cathodic reduction.

In the literature we find mention made of many tungsten oxides. Some of these are:

WO	Black[29]	
WO_2	Brown[30]	purple
W_2O_5	Blue[31]	purple
W_4O_{11}	Blue [32]	green
W_5O_{14}	Green Blue[33]	green
WO_3	Yellow[34]	green

Mixtures of these oxides produce intermediate colors. Brown and blue give purple; blue and yellow give green. These colors agree with the colors obtained by the anodic oxidation of tungsten.

It is obvious that the degree of passivity depends on the nature of the oxide film which covers the tungsten. The brown oxide is less noble than the blue or the yellow.

When the current density is very low and the volume of electrolyte is very large, and the diffusion comparatively rapid, no passivity was observed and no colored films were formed until the electrolyte had become saturated with $W(OH)_6$. Passivity in this case is accompanied by a cloudy precipitate. Passivity is a function of the volume of electrolyte used and the rate at which the anode products are dissolved. The solubility of the anode films was shown by allowing a "passified" anode, which had been thoroughly washed with distilled water after electrolysis, to stand in fresh unused portions of the same electrolyte in which it had been made passive for an hour or two. The time depended on the electrolyte.

A sample of "passified" tungsten became "active" by allowing to stand over night in a tightly sealed bottle of freshly distilled

water. Solution of NaOH, KOH, NH_4OH, etc., make "passive" tungsten "active" almost instantly. The passivity of tungsten is due to a film of adherent oxide or hydrated oxide and is a function of the rate R at which the film is produced and the rate R_1 at which the film is dissolved into the solution used to produce it. If $R = R_1$ we have equilibrium, while if $R > R_1$ the metal becomes passive.

We have found that tungsten dissolves anodically in aqueous solution of NaOH and KOH with the formation of the respective ortho tungstates.

$$W + 6OH = W(OH)_6$$
$$W(OH)_6 + 2NaOH = Na_2WO_4 + 3H_2O$$

Passivity occurs only when the current density is so high that the rate of formation of $W(OH)_6$ is faster than the rate of solution and diffusion in NaOH.

We have found that tungsten dissolves anodically in a solution of HCl (gas) in absolute ethyl alcohol without becoming passive and without the liberation of gas. The anode solution becomes yellow, due to the dissolved WCl_6 and the cathode solution becomes green, due to reduction.[35]

We have found that tungsten dissolves anodically in NH_4OH, NH_2OH, the four methyl ammonium hydroxides, the four ethyl ammonium hydroxides, and propyl ammonium hydroxides within wide limits of current density, without becoming passive. The first product of the reaction $W(OH)_6$ dissolves in the electrolyte to form salts.

Ekeley[36] has found that H_2WO_4 dissolves in amines to form salts which are analogous to $(NH_4)_6W_7O_{24}$. As an example:

H_2WO_4 with $C_2H_5NH_3OH$ forms $(C_2H_5NH_3)_6W_7O_{24}.5H_2O$. His analyses of the salts conform with his formulae.

Electrolyzing $C_2H_5NH_3OH$ between tungsten electrodes produces $(C_2H_5NH_3)_6W_7O_{24}.5H_2O$ at the anode. Analogous salts are obtained with

CH_3NH_3OH; $(CH_3)_2NH_2OH$; $(CH_3)_3NHOH$; $(CH_3)_4NOH$
$(C_2H_5)_2NH_2OH$; $(C_2H_5)_3NHOH$; $(C_2H_5)_4NOH$;
$(C_3H_7)NH_3OH$; $(C_3H_7)_2NH_2OH$.

In NH_4OH, tungsten dissolves anodically with a valence of 6 and 100 percent efficiency to produce ammonium paratungstate $(NH_4)_6W_7O_{24}$. NH_4Cl was added to increase the conductivity of the solution. In conjunction with this experiment, we determined, from the loss in weight of the anode, the electrochemical equivalent of tungsten, and found that when the metal dissolves with a valence of 6, the value of the electrochemical equivalent was 0.3173 mg. per coulomb. The theoretical value calculated from the formula

$$E_W = \frac{\text{At. Wt.}}{\text{Valence} \times 96540} = \frac{184}{6 \times 96540}$$

is 0.3175 mg. per coulomb.[37]

We have found that tungsten also dissolves anodically in NH_2OH. We have not determined the salt formed, but it is probably analogous to ammonium paratungstate.

The anodic behavior of tungsten in aliphatic substitution products of NH_2OH, and the aromatic hydroxyl compounds and substitution products will be discussed in a future paper.

III. THE USE OF W IN CELLS.

Fink[38] mentions the use of tungsten in cells in a paper on "The Applications of Ductile Tungsten," and promises good results both in voltaic and in standard cells. We have since made a further study of these two types of cells and taken up the application of W to storage cells.

Voltaic Cells.

If W is to be used as anode in a voltaic cell, it is desirable to use an electrolyte in which both the tungsten and the anodic reaction products are most soluble. Barring KCN, tungsten is most soluble in solutions of KOH or NaOH. The E.P. W | sol. will be algebraically lowest or in commoner terms the highest — value in NaOH solutions.[39] In addition to the anode it is desirable to have as a cathode a metal, the E.P. of which is a high + value in the same electrolyte (if possible). Hg and Ag are two such metals.

Mercury has an E.P. in a saturated solution of HgO in 1/1 n. NaOH of +0.445 volt[40] compared to calomel = +0.56 volt or — 0.115 volt compared to cal. = O or + 0.168 volt compared to H = O. Silver in a saturated solution of Ag_2O in 1/1 n. NaOH has an E.P. of +0.655 volt[41] when cal. = +0.56 volt or +0.378 volt when H = O. The E.P. W | NaOH is —0.039 volt when cal. = +0.56 volt or —0.316 volt when H = O.

The E.M.F. of the combinations

$$\begin{array}{rl} & \text{Hg} \mid \text{HgO} \mid \text{NaOH} \parallel \text{NaOH} \mid \text{W} \\ \text{and} & \text{Ag} \mid \text{Ag}_2\text{O} \mid \text{NaOH} \parallel \text{NaOH} \mid \text{W} \end{array}$$

will then be respectively

$$\begin{aligned} (+0.445) + \ -(-0.039) &= 0.484 \text{ volt}^{42} \\ (+0.655) + \ -(-0.039) &= 0.694 \text{ volt}^{43} \end{aligned}$$

The mercury and silver are both positive to the tungsten.

To increase the E.M.F. of the cell it is only necessary to increase the concentration of the NaOH solution.

TABLE XIV.

Normality of NaOH	E.M.F. Fused W. Volts	Powdered W. Volts
10	0.595	1.050
5	0.575	1.005
2	0.530	0.920
1	0.484	0.870
0.5	0.440	0.822
.2	0.381	0.777
.1	0.343	0.730
.05	0.315	0.695

The results are very promising with tungsten both as fused slugs and as metal powder. In our preliminary tests the metal powder has given higher E.M.F. values than the fused metal.

Following are readings taken on small experimental cells. The voltage was read across the electrodes of the cell. Resistance was put in series with the cell and the ammeter.

Volts	Amperes	Volts	Amperes
1.05	Open	0.40	0.0640
0.95	0.0057	0.20	0.0850
0.90	0.0120	0.10	0.0950
0.80	0.0220	0.05	0.1000
0.60	0.0430	0.01	0.1020

Other cells in which W enters either as metal or compound are being studied.

Standard Cells.

In connection with the use of tungsten in standard cells we have made the following observations:

TABLE XV.

1.	2.	3.
Electrodes	E.M.F. Volts	E.P. Sol | metal $HgO = +0.445$ Volts
Sat. $Na_6W_7O_{24}$ | $Hg_6W_7O_{24}$ | Hg	—0.401	—0.846
Sat. $Na_6W_7O_{24}$ | $Cu_3W_7O_{24}$ | Cu	—0.235	—0.690
Sat. $Na_6W_7O_{24}$ | W	+0.152	—0.297
Sat. $Na_6W_7O_{24}$ | $Zn_3W_7O_{24}$ | Zn	+0.302	—0.143
Sat. $Na_6W_7O_{24}$ | $Cd_3W_7O_{24}$ | Cd	+0.583	+0.138

Single potential measured with auxiliary electrode

$$Hg \mid HgO \mid NaOH = +0.445 \text{ volt.}$$

Combining these single electrodes one with another we obtained the following combinations which gave the E.M.F. as shown.

TABLE XVI.

$\overset{+}{Hg} \mid Hg_6W_7O_{24} \mid Na_6W_7O_{24}$ sat. $\parallel Na_6W_7O_{24}$ sat. $\mid \overline{W}$	$= +0.552$ volt
$\overset{+}{Cu} \mid Cu_3W_7O_{24} \mid Na_6W_7O_{24}$ sat. $\parallel Na_6W_7O_{24}$ sat. $\mid \overline{W}$	$= +0.395$ volt
$\overline{Zn} \mid Zn_3W_7O_{24} \mid Na_6W_7O_{24}$ sat. $\parallel Na_6W_7O_{24}$ sat. $\mid \overset{+}{W}$	$= +0.154$ volt
$\overline{Cd} \mid Cd_3W_7O_{24} \mid Na_6W_7O_{24}$ sat. $\parallel Na_6W_7O_{24}$ sat. $\mid \overset{+}{W}$	$= +0.434$ volt
$\overset{+}{Hg} \mid Hg_6W_7O_{24} \mid Na_6W_7O_{24}$ sat. $\parallel Na_6W_7O_{24}$ sat. $\mid Cd_3W_7O_{24} \mid \overline{Cd}$	$= +0.981$ volt
$\overset{+}{Hg} \mid Hg_6W_7O_{24} \mid Na_6W_7O_{24}$ sat. $\parallel Na_6W_7O_{24}$ sat. $\mid Zn_3W_7O_{24} \mid \overline{Zn}$	$= +0.703$ volt
$\overset{+}{Hg} \mid Hg_6W_7O_{24} \mid Na_6W_7O_{24}$ sat. $\parallel Na_6W_7O_{24}$ sat. $\mid Cu_3W_7O_{24} \mid \overline{Cu}$	$= +0.134$ volt
$\overset{+}{Cu} \mid Cu_3W_7O_{24} \mid Na_6W_7O_{24}$ sat. $\parallel Na_6W_7O_{24}$ sat. $\mid Cd_3W_7O_{24} \mid \overline{Cd}$	$= +0.831$ volt
$\overset{+}{Cu} \mid Cu_3W_7O_{24} \mid Na_6W_7O_{24}$ sat. $\parallel Na_6W_7O_{24}$ sat. $\mid Zn_3W_7O_{24} \mid \overline{Zn}$	$= +0.537$ volt
$\overset{+}{Zn} \mid Zn_3W_7O_{24} \mid Na_6W_7O_{24}$ sat. $\parallel Na_6W_7O_{24}$ sat. $\mid Cd_3W_7O_{24} \mid \overline{Cd}$	$= +0.283$ volt

The E.M.F.'s of the combinations check up very well with the theoretical E.M.F.'s calculated from the E.P.'s of the single electrodes, Table XV.

These cells are still under investigation and further reports on tests made on their temperature coefficients, life and stability will be given.

Tungsten Storage Battery.

At present we have under investigation several cells made with combinations of tungsten and tungsten oxides.

These cells, A, B, C (Table XVII), were made with tungsten and tungsten acid. The three combinations are shown in the

table. Cell A had tungsten and tungstic acid as the positive electrode and tungsten metal as the negative before charging. Cell B had tungsten and tungstic acid as both electrodes, while Cell C had tungsten-tungstic acid as negative electrode and tungsten as positive, being the reverse of A before charging. The cells were connected in series and charged. The E.M.F. of *each* cell was measured immediately after charging and found to be 3.00 volts for Cell A, 3.20 volts for Cell B, and 6.20 volts for Cell C. Twenty-four hours after charging the cells, the E.M.F.'s had dropped to 0.2 volt, 0.55 volt, and 0.75 volt respectively. The cell having W | WO_2 as positive electrode and W | W_2O_5 as negative electrode after charging has so far been the most satisfactory.

TABLE XVII.

Before Charging.

Type	Positive Electrode	Negative Electrode	E.M.F. Volt
A	W | $WO_3.x\ H_2O$	W	+0.08
B	W | $WO_3.x\ H_2O$	$WO_3.x\ H_2O$ | W	0
C	W	$WO_3.x\ H_2O$ | W	—0.08

TABLE XVIII.

After Charging.

Type	Positive Electrode	Negative Electrode	After Charging E.M.F. Volts	24 Hrs. after Charging E.M.F. Volts
A	W | $WO_3.x\ H_2O$	W	3.00	+0.2
B	W | $WO_3.x\ H_2O$	Blue W | $W_2O_5.z\ H_2O$	3.20	+0.55
C	Brown W | $WO_2.y\ H_2O$	W | $W_2O_5.z\ H_2O$	3.20	+0.75

The results obtained with tungsten storage cells are very promising and will be discussed more fully in a more detailed paper which will follow.

SUMMARY.

1. A brief review of the literature is given.

2. The single potentials of tungsten in 1/1 n. solutions of acids, alkalies and neutral salts were calculated from E.M.F. measurements.

From E.M.F. measurements and calculated E.P. we have found that:

3. Tungsten has a lower single potential in 1/1 n. alkalies than in 1/1 n. acids and a lower single potential in 1/1 n. acids than in 1/1 n. solutions of neutral salts.

4. Tungsten has a lower single potential in KCN solutions than in n. solutions of KOH (or NaOH) and a lower single potential in the latter than in a n. NH_4OH solution. The single potential in KOH (or NaOH) corresponds to that of thallium in a thallium chloride solution containing n. Tl ions.

5. Tungsten has a lower single potential in n. H_2SO_4 than in n. HCl and a lower single potential in the latter than in n. HNO_3. The single potential of W in HNO_3 corresponds to that of Cu in a $CuCl_2$ solution containing n. Cu ions.

6. The order of single potentials of W in n. solutions of neutral salts is as follows, KNO_3,KF, KBr KCl, K_2SO_4, KI, the single potential being highest in solutions of KI.

7. It is shown that in solutions of tungsten in acids, tungsten occurs as cation, whereas in alkaline solutions tungsten occurs in the anion.

8. Tungstic acid is more soluble in n. H_2SO_4 than in n. HCl and more soluble in n. HCl than in n. HNO_3. Direct chemical tests confirm this.

9. Tungstic acid hydrolizes and goes into solution as $W(OH)_6$ in n. solution of H_2SO_4, HCl, HNO_3. W appears in the cation.

10. $W(OH)_6$ is an electrolyte and not a colloid.

11. Tungsten dissolves anodically in aqueous and non-aqueous solutions of alkalies, acids and salts.

12. Tungsten anodes become passive in aqueous and non-aqueous solutions of alkalies, acids and salts.

13. Tungsten becomes passive in aqueous solution of alkalies and organic solutions of alkalies, acids and salts only at very high current densities.

14. Tungsten becomes passive in aqueous solutions of acids and salts even at low current densities. It stays active in these solutions only at very low current densities.

15. The passivity of tungsten is due to adherent films of hydrated tungsten oxides. The films may be readily dissolved and the passivity of the metal thereby destroyed.

16. The hydrated oxide films appearing on the anode vary in color from brown, through blue to yellow. The degree of passivity varies with the color of the film.

17. The passivity phenomena observed can be readily interpreted by the oxide theories of passivity.

18. The electrochemical equivalent of tungsten was found to be 0.3173 mg. per coulomb. This corresponds very closely with the theoretical.

19. Experiments on the use of tungsten in voltaic, standard and storage cells are recorded. The phenomena observed in connection with the storage cell are of particular interest. The potential difference between brown oxide (positive) and blue oxide (negative) is +0.75 volt.

This work was carried out in the Research Laboratories of the Edison Lamp Works of the General Electric Co., under the direction of Dr. C. G. Fink, and finished September 8-9, 1916.

REFERENCES TO LITERATURE.

(1) Zettnow, Pogg. Ann. (1867), **130**, 5.
(2) Hallopeau, Comptes rend. (1898), **127**, 755.
Bull. Soc. Chim. (1898), [3] **19**, 997.
(3) Stavenhagen, Ber. (1899), **32**, 3064.
(4) Scheibler, Jour. prakt. chem (1861), **83**, 322.
(5) Knorre, Zeit. Anorg. Chem. **37**, 125.
Zeit. für Elektrochemie (1903), **9**, 938.
(6) Martin, Zeit. Anorgan. Chem., **65**, 309.
(7) Smith, Ber. (1880), **13**, 753.
(8) Leiser, Zeit. für Elektrochem. (1907), **13**, 690.
(9) Rosenheim, Zeit. für Angew. Chem. (1909), **24**, 1153.
(10) D.R.P. 231657.
(11) D.R.P. 237014.

(12) Fischer, Zeit. Anorg. Chem. (1913), **81**, 170-208.
(13) Fischer, Zeit. Anorg. Chem. (1913), **81**, 102.
(14) D.R.P. 231167, 472167, 35090.
(16) Ostwald-Luther, Physico-Chemische Messungen. Le Blanc, Text-book of Electrochemistry.
(17) Ostwald-Luther, Phys.-Chem. Mess., p. 445.
(18) *Ibid.*
(19) Zeit. Elektrochemie (1903), **9**, 686.
(20-21) Le Blanc, Text-book of Electrochemistry, pages 247-248.
(22) Fischer, Zeit. Anorg. Chem. (1913), **81**, 170-208.
(23) Le Blanc, Text-book of Electrochemistry, page 80.
(24) Dolezalak and Von Ende, Theory of Accumulators.
(25) Bredig, Zeit. Elek. Chem. (1899), **6**, 33.
Zeit. Anorg. Chem. (1903), **34**, 202.
Walker, Zeit. Phys. Chem. (1904), **49**, 82.
(26) Le Blanc, Text-book of Electrochemistry, page 80.
(27) Nernst, Zeit. Phys. Chem (1889), **4**, 129.
(28) Le Blanc and Byers, Zeit. Physik. Chem., **69**, 19.
(29) Fischer, Zeit. Anorg. Chem. (1913), **81**.
(30) Wohler, An. Ch. Ph. (1823), [2] **29**, 43.
Hallopeau, C. R. (1898), **127**, 512.
(31) Scheibler, Z. Chem. (1870), **6**, 212.
Smith, Ber. (1880), **13**, 753.
(32) Leiser, Zeit. für Elektrochemie (1907), **13**, 690.
(33) Desi, Jour. Am. Chem. Soc. (1897), **19**, 213.
(34) Dammer, Handbuch der Anorg. Chem. **III**, S., 636.
(35) Fischer, Zeit. Anorg. Chem. (1913), **81**, 170.
(36) Jour. Am. Chem. Soc., **31**, 6.
Chemical News (1909), **100**, 53.
(37) Richards, Collins, Heimrod, Zeit. Phys. Chem. (1902), **41**, 302.
(38) C. G. Fink, Trans. Am. Elect. Soc. (1913), **17**, 229.
Jour. Ind. & Eng. Chem. (1913), **V**, 8.
Chemical News (1913), **107**, 282.
(39) See Table III.
(40) Ostwald-Luther, Phys.-Chem. Mess.
(41) Ostwald-Luther, Physiko-Chemische Messungen.
(42) See Table III-A.
(43) See Table III-B.

DISCUSSION.

C. G. Fink[1]: One of the disadvantages of lead for battery grids is its low tensile strength. The limiting cross section of the metal of the grid is decidedly smaller in the case of tungsten than in the

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case of lead, so that the total weight of metal for the same amount of energy is smaller in the case of tungsten than in the case of lead, even though the specific gravity of tungsten is higher than that of lead.

F. C. FRARY[2]: It seems to me that sometimes in this paper the terms used and conclusions drawn from the data given are not exactly warranted, and particularly so on page 224. The author says that the experiments were made in order to determine the relative solubility of metallic tungsten in solutions of various electrolytes, and afterward he says that the rate of solution varies with the solvent used. It seems to me this is a very unfortunate confusion of terms. What Mr. Koerner means is that he has attempted to determine the relative s o l u t i o n t e n s i o n and not the s o l u b i l i t y. The solubility of tungsten is zero, or practically zero, in the solution. The solubility of tungstic acid in the different solutions is the number of grams of tungstic acid that will dissolve in one liter. What you measure when you measure the electrode-potential of tungsten in caustic which is not supposed to contain any tungsten in solution, is an index of the heat of formation in solution of tungstic acid from metallic tungsten, under the conditions present. I do not believe we would be justified in assuming that it had a direct relation to the actual solubility of tungstic acid in the caustic. For that reason, I object to the eighth conclusion of the summary which says: "Tungstic acid is more soluble in n. H_2SO_4 than in n. HCl, and more soluble in n. HCl than in n. HNO_3. Direct chemical tests confirm this."

I object to that statement as a conclusion derived from the electrode-potential data. It may be perfectly true, but I object to it as a matter of record. You cannot draw that kind of conclusion from those data.

On page 226 it seems to me that the conclusions in the second paragraph, *viz.*, that "the finely divided black metal contained a lower form of oxide, either as a mechanical mixture, or adsorbed to and covering the metal particles," and that this form of oxide was the cause of the electrode being more negative than some of the other tungsten electrodes, are unwarranted. If we consider the matter carefully, we see that the electrode-potential is a

[2] Research Chemist, Oldbury Electrochemical Co., Niagara Falls.

measure of the heat of formation and solution of the tungstic acid from the metal, but if you have already partially oxidized your tungsten, you cannot get more energy evolved by finishing the oxidation than you could get by starting with the metal and going through to the same oxide. Therefore, this more negative potential must be due to occluded hydrogen, or some special condition of the surface, rather than to occluded oxide, and I do not see how the authors can say in the same paragraph that tungsten oxides are more soluble in caustic and have higher electrode-potentials than tungsten.

In the first place, the "higher potential" is a term we certainly should not use in any way, because it is susceptible of very decided misinterpretation, as to whether we mean a more negative or more positive potential. It is obvious that tungsten itself, as such, is not soluble in caustic, and I fail to see how the conclusion, so stated, could be drawn from the data which the author has given. I think the whole thing, as far as the statements are concerned, is another example of loose use of terms, which I hope as a Society we will oppose as much as possible, because it confuses greatly the people who try to read it.

C. G. FINK: Mr. Frary's remarks are fairly well taken. Yet Mr. Frary must not confuse the problem, or the purpose of the investigation, with the result of the investigation. Mr. Koerner sought to determine the relative solubility of metallic tungsten in solutions of various electrolytes. That was the problem, and on page 226 we state: "Tungsten oxides are more soluble in NaOH than tungsten, and have higher E. P.'s in NaOH than tungsten," If you take a gram equivalent of tungsten oxide and place it in a beaker of sodium hydroxide solution, and take a gram equivalent of tungsten metal, and place it in a beaker of sodium hydroxide, and allow them to stand, stirring occasionally, you will find that the gram equivalent of tungsten oxide has lost decidedly more weight, has gone decidedly more readily into solution, than the tungsten metal, so that it is perfectly proper as stated.

There is a very unfortunate state of affairs in the literature regarding the plus and minus of single potential signs. Prof. Watts and ourselves are not using the same signs in our papers. Where Prof. Watts uses plus we use minus; our notation is that of Ostwald.

O. P. WATTS[3]: I take exception to Mr. Frary's remarks upon the uncertainty of what is understood by the term "higher potential." I can see no reason for Mr. Frary's statement that we are left in doubt when we speak about one metal having a higher potential than another. To me this statement is just as definite as when the temperature of one body is said to be higher than that of another body. If the statement that "zinc has a higher potential than copper" leaves any doubt in Prof. Frary's mind, this can only be due to the iniquitous system which he uses for designating potentials, and his confusion of mind is the condition to which we will all be reduced if we adopt his system.

I must plead guilty—if it be guilt—to speaking of zinc as an electro-positive metal, but I have yet to see a good reason why certain members consider it better to call zinc an electro-negative metal. This is purely a matter of agreement. In the early days of electrochemistry the first electrochemical series commenced with oxygen, chlorine, etc., and these elements were called electro-positive because they were liberated at the positive pole of the electrolytic cell. Sometime between 1847 and about 1860 (I do not know the exact date) the scientific world agreed on a change, and turned the series end for end, calling oxygen electro-negative and sodium, potassium, etc., electro-positive. I am not sure of the reason for this, but it probably arose from the observation that unlike electrical charges attract and like charges repel each other. Having agreed to call the anode the positive pole of the electrolytic cell, it followed that oxygen, chlorine, etc., which are liberated at the anode, should be electro-negative substances. The world accepted this nomenclature until three or four years ago, when certain insurgents commenced to call sodium and potassium electro-negative, and chlorine, oxygen, etc., electro-positive. The resulting confusion, which Prof. Frary himself acknowledges, is certainly greatly to be deplored.

I would urge that this Society take some action to prevent the calamity of a dual system for designating potentials. If those who are in favor of this revolution can give good and sufficient reasons which will satisfy the scientific world that this change will be a great benefit, that it expresses better than the system of potentials now generally used, the flow of current through the various parts

[3] Assistant Professor of Applied Electrochemistry, University of Wisconsin.

of the electric circuit, then let us by all means adopt it. But if the change does not promise some great gain to electrochemistry to offset the trouble and confusion which it will inevitably cause, it seems to me that we had better retain the nomenclature which has been in use for a half-century, and thus avoid having two ways of writing potentials in use for many years to come, with the final result of rendering unintelligible to the electrochemist of the future nearly all of the literature so far written concerning potentials. The burden of proof lies with the gentlemen who would change the present system of designating the potentials of metals and of the electrodes of the electrochemical cell.

CARL HERING[4]: The discussion concerning positive and negative is interesting. Formerly we thought of electricity flowing from the positive pole to the negative pole, which conception we have been using for over a century. But recent developments have shown that it is the negative and not the positive electrons which are the ones that move, and in the opposite direction. Hence, formerly a loss of a charge meant that it was a positive charge, while today, in order to conform to modern developments, we must refer to the negative charge as the unit, which, of course, reverses everything. It is a question whether we shall adopt the new method or adhere to the old.

My own views on this subject are expressed in an article which appeared in the May 1st issue of Metallurgical and Chemical Engineering.

W. R. MOTT[5]: I want to question Dr. Fink as to the conductivity of these various oxides, especially WO and WO_2, because in any electrolytic cell the conductivity of the products of the electrolysis plays a very vital part in the voltage efficiency. Was the high voltage twelve volts?

C. G. FINK: Yes, twelve volts.

W. R. MOTT: How many cells?

C. G. FINK: One cell, directly after charging.

W. R. MOTT: It is rather unusual to get a voltage like that. What was the charging voltage?

[4] Consulting Electrical Engineer, Philadelphia.
[5] Research Laboratory, National Carbon Co., Cleveland.

C. G. FINK: The charging voltage was about twenty volts. There was appreciable gassing.

W. R. MOTT: The only case I recall personally of having obtained such a large voltage, outside of the aluminum cell type of phenomenon, was in the case of a rubber diaphragm of thin membrane. This had a very high discharge voltage, polarizing with 110 volts. There might be some diaphragm effect or high resistance layer.

F. C. FRARY: In regard to the matter of the potential signs, I think the whole matter is a confusion between our statement as to a metal being electro-positive or electro-negative, and the sign of the electrode-potential of that metal in contact with a solution. I think we will all agree with the general statement, for instance, in respect to sodium chloride, that sodium is the electro-positive metal and chlorine is electro-negative, and we accept the sodium ion as having the positive charge and the chlorine the negative in a solution. I wonder if, having a sodium electrode in any solution, the sodium electrode would become positive to the solution. That is virtually what Dr. Watts said in his paper, when he gives these things the reverse sign.

The electrode potential of a substance in a solution is determined by the reaction between that substance and the solution. Suppose we put zinc in sulphuric acid, we find there is a difference of potential between the two, and if we measure it we find the zinc is actually negative to the solution. We explain this by saying that the zinc has sent particles (ions) into solution, and they become electrostatically charged, positively, giving negative electrons to the electrode, and the electrode therefore becomes negative to the solution.

Years ago there were some persons who preferred to give the electrode-potentials in the form of the potential of the solution minus the potential of the electrode; but it has been generally agreed recently that when we say that the electrode potential of the metal is plus or minus, we mean the potential of the electrode minus the potential of the solution. If we look at it in that way, the value which Dr. Fink is using for the calomel electrode, plus 0.560, means that the mercury is positive to the solution, as it actually is, while the value Dr. Watts uses, minus 0.560, is such

that his results come out with the wrong sign. This means that Dr. Watts is looking at it from the other end, that is to say, he thinks the electrode-potential of the electrode in solution is the potential of the solution minus the potential of the electrode. I believe I am correct in saying that with the exception of one or two misguided authors of text-books, every one else, present company excepted, agrees that the electrode potential of the metal is the potential of the metal minus the potential of the solution, and I think that system should be followed consistently.

O. P. WATTS: I feel that possibly I had better say a word or two more in defense of my position. Those gentlemen who are contending for the classification of zinc as electro-negative will get into conflict with our electrical engineers and a great many other engineering people. We use the term positive to designate that material from which the current flows to something else that is negative, like the flowing of water down hill, like the flowing of heat from the point of higher temperature to the point of lower temperature, and the positive and negative signs are always used in that way in dealing with the flow of heat. Two bodies, one having a more positive temperature than the other, may both be below zero, so that both might be thought of as negative bodies, but the flow of heat always takes place from the more positive to the more negative, and we use the terms "positive" and "negative" throughout all our language in that sense.

Now, these gentlemen appear before us and ask that we consider the flow of electric current as taking place from the negative to the positive metal. Let us consider the gravity cell from their viewpoint. They would have the current flowing from the electro-negative zinc to the electro-positive copper, through the electrolyte, yet passing through the ammeter from positive to negative. It seems to me bad usage to employ any terms which would bring about such a situation. I think it vastly better to stick to the old terms under which we conceived of the zinc as the electro-positive body, and the current as flowing in the electrolyte from the electro-positive zinc to the electro-negative copper; then we have the flow of current in every part of the circuit taking place from positive to negative.

CARL HERING: We must admit, unfortunately, that Franklin, Volta, Galvani or whoever it was who first defined positive and negative electricity and stated that the current flowed from the plus to the minus, guessed wrong. It does not flow that way, it flows the other way. The question arises, shall we go on making that mistake, or shall we rectify it? Some day we may have to rectify it, although we have a precedent for continuing to make a similar mistake when we say for convenience that the sun rises, while we know that it does not.

F. C. FRARY: There is one point I did not answer—the remarks about the higher and lower temperature. I am glad Dr. Watts said what he did, because as I understand him he agrees that 10 degrees below zero in one room is higher than 20 degrees below in the next room, although numerically the number which represents it is the other way. My objection to the use to which the terms can be put is exactly on that ground. We ordinarily understand by a higher temperature, or anything higher, a tendency to be more positive.

In Dr. Watts' paper, he says very definitely on page 305: "It is in this tendency to deposit only the element of lower potential when the difference of potential is great," referring to the co-deposition of copper and hydrogen, where copper has a potential which is actually less electro-negative than the potential of hydrogen. In that case he is using his terms in exactly the opposite sense to that in which he has just used them here. I object to the wholesale use of lower and higher in this connection, just for that reason, as it is likely to lead to misunderstandings and mistakes.

In regard to the question as to whether zinc is electro-negative or electro-positive in the dry battery, I would suggest that if Dr. Watts thinks it is electro-positive he might try it with a voltmeter.

O. P. WATTS: In connection with this discussion, Dr. Frary overlooks the fact that electricity flows in a closed circuit, like a wheel spinning around its axle, if the lower part of the rim is moving in one direction the top part must move in a contrary direction; the same is true of an electric circuit. In the voltaic cell the current flows through the cell from zinc to copper. If you put a voltmeter on the cell, you must of necessity attach the

positive of the voltmeter to the copper plate to receive the current which flows around in this direction.

In regard to the statement that I was confused in the matter of copper and hydrogen potentials, I will explain that Mr. Frary exchanged my numbers and then accused me of being confused.

W. R. MOTT: I make a motion that a Committee be appointed by the President to look into this matter of nomenclature (of single potentials with reference to polarity and zero of reference) which is vitally important to our progress, and such Committee set forth what they consider a standard nomenclature which can be recommended by our Society, the Committee to consist of three or five or whatever number the President desires. In my experience in looking over thermo-electric data this same wheel effect comes in, with much contradiction as to polarity direction. In regard to single potentials, no one knows where the zero of reference belongs. The selection of the zero of reference is unfortunately widely different, and this makes much data almost worthless, because it is so difficult to co-ordinate with other data. I suggest that in writing a paper it is highly desirable to give some well-known point, say zinc, of which we know the potential, so you can tally backwards and properly interpret the nomenclature.

F. A. LIDBURY: I second the motion.

CARL HERING: I move, as an amendment, that the Committee be requested to report at the next general meeting of the Society.

W. R. MOTT: I accept the amendment.

(The motion was put to vote and carried).

C. G. FINK: In a communication which I received from Prof. Watts it is shown that the whole surface tension phenomena and the capillary electrometer results obtained fit in so nicely with the nomenclature which Dr. Frary and myself are in favor of, that I think Prof. Watts will eventually agree with us. Prof. Watts will probably serve on the Nomenclature Committee, and we shall await its report with interest.

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 5, 1917, President FitzGerald in the Chair.

ELECTRICAL ENDOSMOSE AND ADSORPTION.

By T. R. Briggs, H. L. Pierson and H. S. Bennett.

[*Abstract.*]

The relations are discussed between electrical endosmose and the adsorption theory of contact electrification. It is shown that this theory provides a rational explanation of the phenomena. The data accumulated by Perrin are found to be confirmed by the author's experiments. The effect of temperature on the phenomena is studied in detail. Finally, the phenomena met in dyeing are discussed from the standpoint of the adsorption theory, and found to be in accord with the details of the theory.

When a porous diaphragm divides a liquid into two portions and a potential gradient is established within the system, a flow of liquid tends to occur through the dividing septum. Sometimes the flow is to the cathode; at other times the flow appears to take place in the opposite direction. The phenomenon is called *electrical endosmose,* and should not be confused with *cataphoresis,* which refers to the electrical migration of a solid suspended in a liquid. Electrical endosmose, cataphoresis, and other closely related effects are measures, with certain very definite limitations, of the contact potential differences which may exist at the interface between solid and liquid. According to the Quincke-Helmholtz theory, solid and liquid are charged oppositely by contact, and the charged liquid, being free to move, flows to one electrode or the other when placed under the influence of an electric field (potential gradient).

The mechanics of electrical endosmose are fairly well understood, but we are still more or less in the dark regarding the difference of potential at the solid-liquid interface. For certain so-

called "pure" liquids, Coehn[1] has proposed the empirical rule that when solid and liquid are in contact the substance with the higher di-electric constant is charged positively with respect to the other substance. On the other hand, Perrin[2] has shown that one may often reverse the sign of the charged solid by adding to a neutral liquid traces of acid or base, or by introducing certain other substances. In view of these results of Perrin, many of Coehn's experiments are open to serious objections, and should be repeated.

Perrin found that solids tend to become positive in acid solutions and negative in alkaline solutions. Furthermore, the contact potential is influenced strongly by very small concentrations of the active hydrogen and hydroxyl ions. It was shown also that certain cations reduce the negative charge produced in an alkaline solution and that certain anions lower the positive charge due to an acid solution. The Schulze valence rule holds for the particular ions that Perrin studied, though Elissafoff,[3] working in Freundlich's laboratory, showed later that there are many exceptions.

Some years ago Bancroft[4] pointed out that the most satisfactory working hypothesis to explain electrical endosmose and contact electrification was the one suggested originally by Freundlich[5] and based upon the preferential adsorption of anions or cations by the solid composing the diaphragm. If the solid adsorbs cations preferentially it becomes positively charged, and the liquid, accordingly, flows to the anode under the influence of a potential gradient through the diaphragm. Preferential adsorption of anions renders the solid negative.

We start with the properties of surfaces. By virtue of these properties solids are able to adsorb substances from a liquid with which they are in contact. They may adsorb a particular ion preferentially, in which case we have selective ion adsorption and either a positive or negative charge on the solid. The adsorbing substance tends to be peptized by the adsorbed ion. Or solids may adsorb the solvent itself and be peptized, whilst the other

[1] Wied. Ann. (1898) **64**, 27; Zeit. Elektrochemie (1910), **16**, 586.
[2] Jour. Chim. phys. (1904), **2**, 601.
[3] Zeit. phys. Chem. (1912), **79**, 385.
[4] Jour. Phys. Chem. (1812), **16**, 312; Trans. Am. Electrochem. Soc. (1912), **21**, 233.
[5] Kapillarchemie (1909), 245; Zeit. phys. Chem. (1912), **79**, 407.

possibilities are adsorption of a non-electrolyte, an undissociated salt, or a second colloid. Since electrical endosmose has to do with electrically charged surfaces, we are concerned now chiefly with preferential ion-adsorption.

We postulate that every solid has a specific adsorbing power for a given ion, which depends upon the specific surface[6] of the solid, upon the temperature, upon the concentration of the particular ion in the solution, and upon the other ions present in the solution or previously adsorbed by the solid. When the ion content of a liquid is vanishingly small, we shall have but little ion adsorption and little electrical endosmose. Non-dissociated and non-dissociating liquids have been shown by Perrin to exhibit no electrical endosmose. On the other hand, the purest water shows the phenomenon, and here one must postulate preferential adsorption of hydrogen or hydroxyl ions from water itself or adsorption of ions formed by the dissolving of the solid material of the diaphragm.

The general case is where one is dealing with a solid diaphragm in contact with liquid containing ions. We shall formulate the adsorption theory as follows:

(1) Electrical endosmose depends upon the preferential or selective adsorption of ions and is influenced only by those ions which are adsorbed by the diaphragm.

(2) A diaphragm tends to become positive by the preferential adsorption of cations and negative by the adsorption of anions.

(3) Any circumstance or condition which changes the adsorption produces an effect upon electrical endosmose. Electrical endosmose varies, therefore, with the condition of the surface (for a given solid), with the relative and absolute ion concentrations, with the temperature, and so forth.

(4) The *direction* of the endosmotic flow indicates the sign of the diaphragm; the *rate* of flow is proportional to the intensity of the charge on the diaphragm, in case the potential gradient through the diaphragm is constant. When the liquid flows to the cathode, the diaphragm is *negative;* when it flows to the anode, the diaphragm is *positive.* No flow at all indicates an iso-electric condition.

[6] Surface per unit volume or unit weight.

(5) The positive charge produced by an adsorbed cation is neutralized more or less by the addition of an adsorbed anion, the effect increasing with the concentration of anion. Similarly, the negative charge produced by an adsorbed anion is neutralized by an adsorbed cation.

(6) Electrical endosmose measures the tendency of a solid to form an electrical suspension in a given liquid, but it does not measure the tendency of the solid to form a non-electrical suspension such as is produced by adsorbed solvent, salt or second (neutral) colloid.

Since it is probable that electrical endosmose can occur only when the liquid contains ions which are adsorbed by the solid, in considering the case of pure liquid and the Coehn rule we must not neglect the following points, when, as is usual, water is the liquid under consideration:

(1) The specific adsorption capacity of the solid for hydrogen and hydroxyl ions produced from the ionization of water.

(2) The solubility of the solid itself, which, though extremely slight in most cases, may produce ions which are strongly adsorbed.

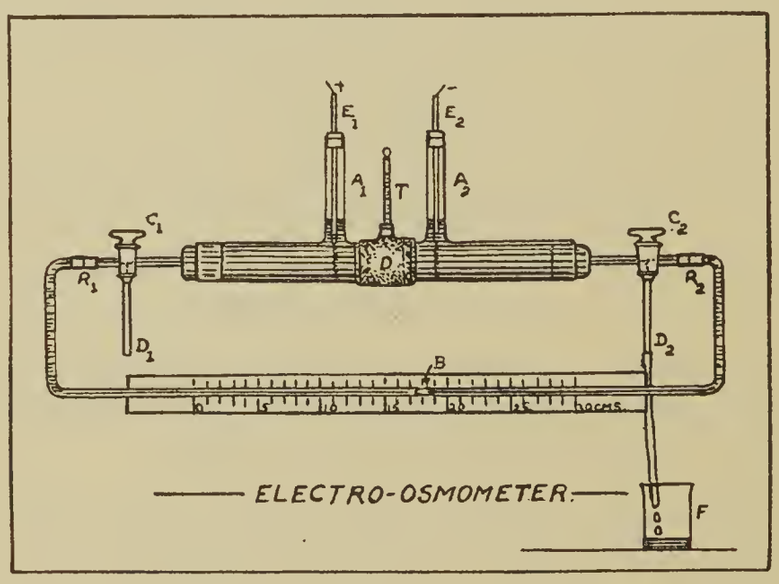

FIG. 1.

EXPERIMENTAL.

The apparatus developed after a great deal of experimenting is a modified form of Perrin's endosmometer, but has the advantage over the latter of eliminating the error produced by evolution of

gas at the electrodes. The apparatus is so designed that one may easily introduce a diaphragm of any suitably powdered solid and may measure the direction and rate of endosmose by observing the motion of an air bubble in a horizontal tube connecting the anode and cathode chambers.

It has been shown theoretically and mathematically that for a particular diaphragm of constant length (l) and cross section (q) the volume of liquid transported in unit time is proportional directly to the external potential applied (E), to the interface

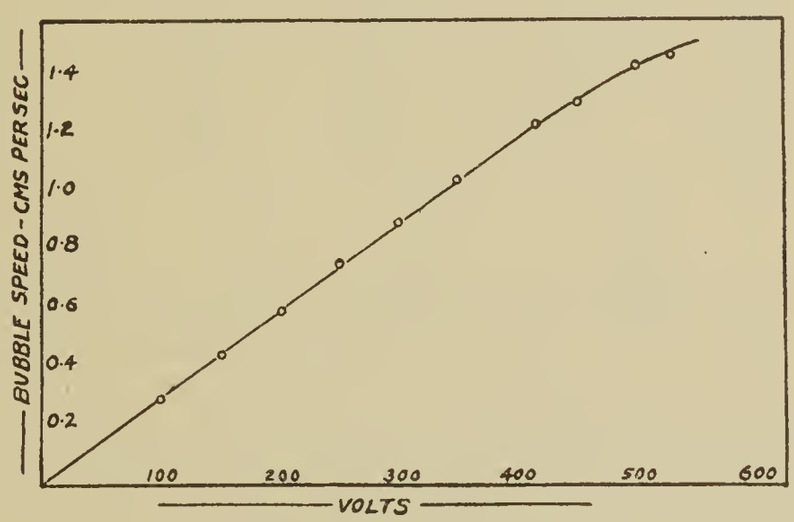

FIG. 2.

potential (ϵ), to the di-electric constant of the liquid (D) and inversely to the viscosity coefficient (η) of the liquid. These relationships are stated in the following formula:

$$V_e = \frac{q \epsilon E D}{4 \pi \eta l}$$

Certain preliminary determinations were made to test this formula. With a given diaphragm at constant temperature the effect of varying the applied voltage was ascertained. The diaphragm was of glass, powdered so as to pass an 80-mesh sieve and be retained by one of 120 mesh. It was held in position by glass wool, and distilled water was used as the liquid. By means of a small 0.11 K.W. generator operated by an induction motor, the current from a battery of storage cells could be transformed to any desired voltage up to 500. The very excellent data obtained are illustrated in Fig. 2 by means of a curve drawn between voltage and speed of the indicating bubble.

TABLE I.

Influence of Applied EMF on Rate of Flow.

Glass diaphragm in distilled water. Liquid flowed to cathode.

Applied Potential Volts	Time sec.	Distance cm.	Temp. ° C.	Rate cm. per sec.	Rate/Potential
530	13.5	20	19.8	1.48	27.9
500	13.8	20	19.9	1.45	29.0
450	15.2	20	19.8	1.32	29.3
416	16.1	20	20.0	1.24	29.8
350	19.1	20	20.5	1.05	30.0
300	22.2	20	19.7	0.90	30.0
250	13.2	10	19.6	0.76	30.4
200	16.8	10	19.7	0.60	30.0
150	22.0	10	19.6	0.45	30.0
100	32.8	10	19.5	0.30	30.0

The effect of temperature at constant voltage was studied next, since the literature is full of conflicting statements[7] regarding this point. When diaphragms of powdered glass were used, the results obtained were hopelessly irregular. One often obtained maximum bubble speeds as the temperature rose between 20° and 65° Centigrade. Starting with distilled water, it was found that the conductivity of the latter increased rapidly as the experiment continued, especially at the higher temperature. The glass of the diaphragm and the plugs dissolved so appreciably that the composition of the liquid was no longer the same as in the beginning and the contact potential was no longer approximately constant, as it probably would be for small temperature changes, since adsorption is not greatly affected by changes of temperature.

Glass was eliminated as much as possible by using carborundum and alundum diaphragms held in position by small plugs of cotton wool, washed asbestos, or macerated filter paper. The distilled water was kept in contact with the diaphragm for at least 24 hours to insure equilibrium. The results confirmed the fundamental equation most satisfactorily, for it was shown that the rate of electrical endosmose increased with the temperature slightly less rapidly than did the reciprocal of the viscosity coefficient. The data of Table II illustrate this point.

[7] See Perrin: Jour. Chim. phys. (1904), 2, 601; Coehn and Raydt; Drude's Ann. (1909), 30, 797; Cameron and Oettinger; Phil. Mag. (1909) [6] 18, 386; Cruse: Phys. Zeit. (1905), 6, 201.

TABLE II.

Influence of Temperature at Constant Voltage.

Asbestos diaphragm. Distilled water. Flow to cathode.

Applied Potential Volts	Time sec.	Distance cm.	Temp. ° C.	Rate cm. per sec.	Rate times viscosity 10^{-4}
250	16.2	5	18.0	0.308	32
250	25.9	10	30.5	0.386	31
250	22.0	10	39.0	0.454	30
250	19.8	10	46.5	0.505	30
250	18.0	10	58.0	0.588	30
Cellulose in *boiled* water (air free).					
400	28.2	5	22.6	0.177	16.7
400	25.5	5	27.6	0.196	16.7
400	22.3	5	36.1	0.224	15.9
400	19.1	5	52.0	0.262	14.0
400	17.1	5	67.0	0.292	12.5

Since the rate of endosmose is proportional directly to the applied voltage and is inversely proportional, approximately at least, to the viscosity coefficient (fluidity) of the liquid at the temperature of the experiment, it is possible to reduce, by means of an equation, the bubble speed at any temperature and voltage to standard conditions, which we have taken arbitrarily to be 20° Centigrade and 100 volts. The formula follows:

$$\text{Corrected rate} = \frac{\text{observed rate} \times 100 \times \eta_{t^\circ}}{E \times \eta_{20^\circ}}$$

In the experiments which follow, this correction for temperature and voltage variations has been made in all cases.

Electrical Endosmose with Acid and Alkaline Solutions.

A set of experiments was carried out in Worcester by Mr. Pierson, for the purpose of duplicating Perrin's results with dilute solutions of acids and bases. Using a diaphragm of 120-mesh crystolon, supplied by the Norton Company, the following data were obtained, which are pictured in Fig. 3. It will be noticed that the results confirm Perrin completely, and that the curve

obtained is similar to one drawn by Freundlich[8] from Perrin's data. The reversal of flow is sharply defined, and the iso-electric point lies over on the acid side at concentrations of hydrochloric acid less than one-thousandth normal. Similar data were obtained with alundum. When powdered glass was studied, however, the flow was always to the cathode and no reversals were obtained in acid solutions, though the rate of flow to the cathode became less as the acidity increased. Acid-alkali reversals were obtained with diaphragms of gelatine and agar jellies.

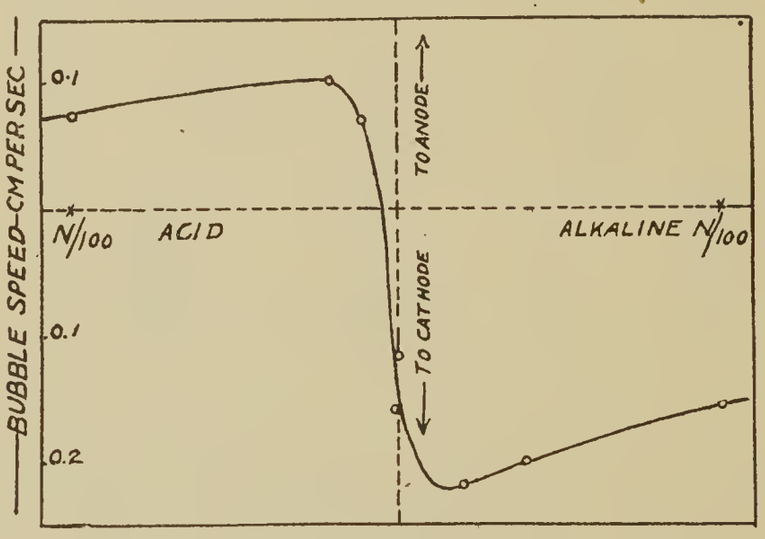

FIG. 3.

Effect of Certain Polyvalent Ions.

A long series of experiments again confirmed Perrin, by showing that many polyvalent ions exert a marked influence on the direction and magnitude of electrical endosmose. Barium salts furnished typical divalent cations, alkali sulphates furnished typical divalent anions. Alundum and carborundum were used as diaphragms. In alkaline solutions adsorbed barium ions reduced the rate of electrical endosmose to the cathode much more than did an equivalent of alkali metal cation. In acid solution barium is without much effect, for here adsorbed anions lowered the rate, sulphate being much more effective than chloride, nitrate or acetate.

Effect of Copper Salts.

A study of electrical endosmose with solutions of copper salts and an alundum diaphragm showed that in neutral solutions copper nitrate, chloride and acetate flowed to the anode, while copper

[8] Kapillarchemie (1909), 236.

sulphate, as it became more concentrated, flowed to the cathode. This would indicate that copper as ion is adsorbed more readily than acetate, chloride or nitrate (hence a positive charge on the alundum), but less readily than sulphate when the solution is somewhat concentrated. These data account for copper sulphate going to the cathode through a porous cup whilst copper nitrate goes to the anode.[9]

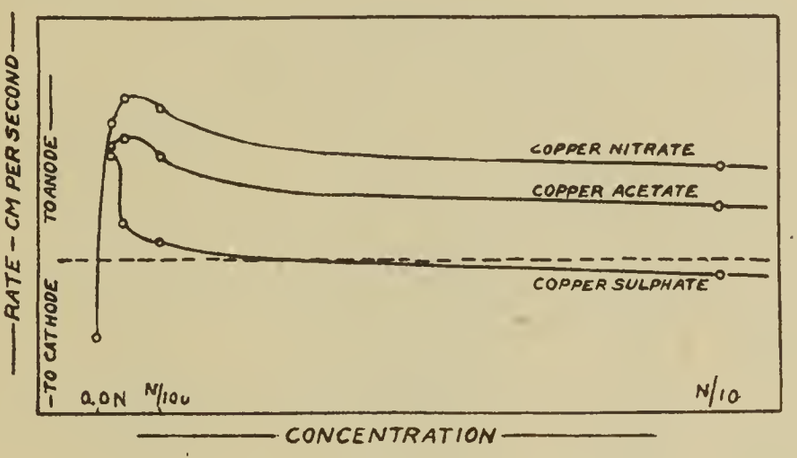

FIG. 4.

Electrical Endosmose and Dyeing.

Bancroft[10] has discussed the theory of dyeing from the point of selective and specific adsorption. So far as known, the adsorption of a dye by fibers or mordants depends, for a given adsorbent, upon the nature of the dye, its concentration, the other substances present in the dye liquor, as well as upon the temperature. One may define a basic dye to be one having the color in the basic radical, and an acid dye as one having a colored acid radical. For the particular case of an acid dye, we have the following rules:

(1) The dye is taken up most readily in an acid solution, but may be taken up in a neutral or alkaline solution.

(2) A readily adsorbed anion decreases the amount of dye taken up.

(3) A readily adsorbed cation increases the amount of dye taken up.

For the case of a basic dye, the same rules hold, if one substitutes "alkaline" for "acid" and "cation" for "anion" and *vice versa*. A basic dye is taken up most readily in an alkaline solu-

[9] Coehn: Zeit. Elektrochemie (1910), **16**, 586.
[10] Jour. Phys. Chem. (1914), **18**, 1, 118, etc.

tion. After all, rule (1) above is only a special case covered by (2) and (3), and would fail to hold in case the hydrogen ion of a particular acid were less readily adsorbed than its anion.

Mr. Pierson carried out a series of experiments designed to test the first of these generalizations. Alundum diaphragms were used and the following data obtained:

TABLE III.

Acid and Basic Dyes.

Dye	Nature of Dye	Solution (approx.)	Rate (corrected) (Cm. per sec.	Direction
Eosine	acid	N/500 HCl	(very slow)	?
Eosine	acid	N/500 NaOH	0.092	to cathode
Crystal ponceau	acid	N/500 HCl	(very slow)	?
Crystal ponceau	acid	N/500 NaOH	0.059	to cathode
Safranine	basic	N/500 HCl	0.077	to anode
Safranine	basic	N/500 NaOH	(very slow)	?
Methylene blue	basic	N/500 HCl	0.022	to anode
Methylene blue	basic	N/500 NaOH	(no flow)	?

(In each case concentration of dye was approximately N/5000).

The results are quite in accord with the theory, and they emphasize certain points—particularly the marked effects which traces of dye may produce and the differences which characterize acid and basic dyes. Alundum behaves, as mordant, essentially like hydrous alumina, except that the amount of dye removed by alundum is small and the dyed material is not fast to washing. When crystal ponceau was used in alkaline solution it was easily removed from the diaphragm by washing; after the dye was used in acid solution, however, it could be washed out only with difficulty. Methylene blue displayed the opposite behavior, for it was washed out easily when it had been used in acid solution but was removed with difficulty when it had been used with alkali.

The experiment is an excellent illustration of the neutralization of adsorbed ions. Alundum adsorbs hydrogen ions from an acid solution and becomes positively charged. If one adds a basic dye neutralization of the adsorbed hydrogen can occur only by the adsorption of the colorless acid radical (usually chloride), which we have found by experiment to be only slightly adsorbed. Some neutralization does occur, because the concentration of anions has

been increased by adding the dye. But when we add an acid dye, the colored acid radical is adsorbed and the positive charge on the diaphragm is neutralized. The adsorption of a basic dye from an alkaline solution is another case of neutralizing an adsorbed ion (hydroxyl).

The results of this paper may be summarized as follows:

(1) The importance of the adsorption theory of contact electrification and electrical endosmose has again been emphasized.

(2) A new and convenient apparatus has been devised for measuring accurately electrical endosmose.

(3) Perrin's data have been confirmed in all essentials.

(4) The effect of temperature has been studied in detail.

(5) The relationship between dyeing and electrical endosmose tends to confirm the adsorption theory.

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DISCUSSION.

J. W. RICHARDS[1]: In electrolyzing H_2O_2, hydrogen peroxide, an increase of volume of the cathode liquid, the catholyte, is very much in evidence. It is extremely rapid. It is so rapid that the first time it occurred in my tests, with a closed partition between the anode and cathode, the anode compartment went dry before we noticed what was happening; the liquid had almost all gone into the cathode compartment. I made a rough quantitative estimate of the amount of water which might be assumed to have traveled with the hydrogen in one direction and the oxygen in the other; of course, we had only the difference. If we assume the ions are hydrated and already combined with the solvent, and therefore passing in two opposite directions combined with different amounts of the solvent, we would have the assumed hydrated hydrogen ion carrying with it about 50 more molecules of water into the cathode compartment than the oxygen ion takes in the opposite direction. This gives a vivid idea of the very high degree of hydration of the ions in solution.

[1] Professor of Metallurgy, Lehigh University.

CARL HERING[2]: There is another feature of interest in electrolyzing H_2O_2. I made some tests and found for a time absolutely no gas formed on one electrode; one would gas freely and the other would not gas at all.

J. W. RICHARDS: If it is electrolyzed quantitatively, and you make measurements as to how much hydrogen peroxide decomposes in one compartment over another, and measure the amount of gas you have in such compartments, you find you get half the normal amount of hydrogen and double the normal amount of oxygen, calculated as in the normal electrolysis of a sulphuric acid solution.

F. A. LIDBURY[3]: Is that independent of current density, or did you just take the experiments at one particular current density?

J. W. RICHARDS: One current density.

F. A. LIDBURY: It would be interesting to observe whether the ratio persisted with changes of electrolytic conditions. It is probably just an accident.

J. W. RICHARDS: I intended to submit a short paper on this subject for this meeting, but did not have time to repeat the results. The experiment was made twice, but the results were not definite enough to present in a paper. My own interpretation is that the hydrogen is evolved as a divalent element.

F. A. LIDBURY: Possibly the explanation of the deficiency in hydrogen at the cathode is that the hydrogen peroxide is reduced. If there is a regular evolution of fifty percent of the normal quantity of hydrogen, that might have some significance in the sense Prof. Richards suggests, but in order to establish that fact, the effect of varying concentrations at varying temperatures and varying current densities would have to be investigated, otherwise it might be simply an accident, and simply happen to give 50 percent under the particular conditions used.

O. P. WATTS[4]: It seems to me that what Mr. Lidbury has just said is the key to the situation, that the current density and the concentration are the two factors which determine the amount of hydrogen which will disappear. It is simply a case of an

[2] Consulting Electrical Engineer, Philadelphia.
[3] Works Manager, Oldbury Electrochemical Co., Niagara Falls, N. Y.
[4] Asst. Professor of Applied Electrochemistry, University of Wisconsin.

oxidizing agent being placed around the cathode, and similar effects can be secured with nitric acid, sodium nitrate, and various other oxidizing agents. At first no hydrogen appears, but as the current density is increased hydrogen is plated out faster than the oxidizing agent can take care of it, and the excess of hydrogen, beyond that which unites with the oxygen will appear as a gas. It is an easy prediction to make that when Dr. Hering consults his experimental data, it will be found to be the cathode at which less than the normal amount of gas appears, due to the presence of the oxidizing agent.

J. W. RICHARDS: I made two experiments with the same current density and under nearly the same conditions, and they gave about the same results. I should be very glad if any one here who cares to look further into these experiments will do so, and if they have the time, do it exhaustively, and try to confirm or contradict these results.

F. C. FRARY[5]: In that connection there is another interesting phenomenon which might be worthy of some one's investigation, which I observed at one time in doing some work on the electrolytic deposition of zinc from a sodium zincate solution. It is relatively easy to deposit zinc from caustic soda solution, but if you take a sample of brass, and deposit the lead and copper electrolytically, and then take the residue, after evaporating, and adding caustic soda, attempt to deposit the zinc under the usual conditions, with a nickel cathode and platinum anode, you sometimes find that suddenly the evolution of gas completely ceases at both electrodes. You can pass as high as three or four amperes through the solution for some minutes, with absolutely no evolution of gas at either electrode. Apparently there is no deposition of zinc on the cathode, no hydrogen from the cathode, no oxygen from the anode. I tried some substances which I suspected might be present as depolarizing agents, and was not able to get the effect by adding any of them. The phenomenon could be made to recur at will by increasing the current for three or four minutes to five amperes, and then dropping it to three, when the evolution of gases would cease and the current would flow as though we had metallic conduction, although, of course, we did not.

[5] Research Chemist, Oldbury Electrochemical Co., Niagara Falls, N. Y.

H. H. WILLARD[6]: I would like to call attention to a peculiar phenomenon I have often observed in the electrolytic determination of nickel which has been precipitated by dimethylglyoxime, the precipitate dissolved in nitric acid, evaporated to fumes with sulphuric acid and the solution rendered ammoniacal, as usual. Out of a class of thirty there will usually be two or three who will obtain solutions from which no nickel is deposited, or at most only a few milligrams, even though the current density is high and the electrolysis continued for hours. Duplicates run parallel with them behaved normally. I have never found any explanation for it, and these conditions cannot be duplicated at will. If anyone can suggest an explanation I should be glad to hear it.

CARL HERING: I described certain electrolytic experiments fifteen years ago, in which I showed that there was apparently metallic conduction, but a little investigation showed it was not metallic conduction; nevertheless, the two electrodes were perfectly dry, no deposits of any kind, and no evolution of gas.

H. H. WILLARD: There is an evolution of gas in this case but no metal is deposited, and in some ways it acts much like metallic conduction. Duplicates, from one of which no nickel is deposited, while the other gives a good deposit, appear alike.

W. R. MOTT[7]: In regard to electrolysis of a solution simulating metallic conduction, I have found a very good one to be a mixture of ferrous sulphate and ferric sulphate, which gives almost no polarization with platinum electrodes, whereas with most water solutions the polarization necessarily will be above one and one-half volts. It will give exactly the same single potential at each electrode, and considerable current can pass with very little polarization.

Going back to the paper, I think this is one of the most fertile fields of electrochemical research, and one of great importance.

Theoretically, I believe there should be a connection between endosmose and static electricity. I do not know whether there is a relation between what we call the migration of ions and osmosis, but this might be worthy of consideration also.

[6] Asst. Professor of Chemistry, University of Michigan.

[7] Research Laboratory, National Carbon Co., Cleveland.

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 5, 1917, President FitzGerald in the Chair.

ESSENTIAL OILS AS ADDITION AGENTS IN PLATING BATHS.

By F. C. Mathers and A. B. Leible.

[*Abstract.*]

Squares of sheet metal were shaken with aqueous solution of the oils, and the amount adsorbed determined by difference by titrating the residual solutions. The metals adsorb oil in decreasing order as follows: lead, antimony, copper, cadmium, zinc, iron, tin, silver. This is approximately the order of increasing difficulty of preventing rough crystalline deposits by the use of the addition agents, and therefore proves in a general way the relation between the effect of the oils as addition agents and their adsorption by the metals.

The generally accepted theory of the action of organic addition agents in the electro-deposition of metals assumes that the addition agent is adsorbed by the metal which is being deposited. If this theory is true, the effective addition agents should be adsorbed more readily than the less effective agents, unless much smaller quantities of the effective agents are necessary to produce the desired result.

The object of this research was to test this idea by determining the adsorption of essential oils by metals. The general scheme of the experiments was to treat a known area of the metals with an aqueous solution of the oil of known strength. A titration of the aqueous oil solution before and after the treatment with the metal gave the quantity of oil which was adsorbed.

QUANTITATIVE ESTIMATION OF THE ESSENTIAL OIL.

After many experiments the following method was adopted for the determination of the oil in solution. Since the method depends upon the oxidation of the oil with permanganate, only those

oils having a marked reducing action can be determined in this manner. Ten c.c. of the aqueous oil was pipetted into a flask; 5 c.c. of 1:10 sulphuric acid was added with 30 c.c. of N/10 potassium permanganate solution and the whole allowed to stand for 24 hours. Then an excess of standard hydrogen peroxide was added, and the titration was finished with potassium permanganate. By this method one drop of the permanganate produced a fairly permanent end point, the pink color persisting even after standing for ten minutes. Independent titrations by this method gave good agreement. The main precautions to be observed are:

1. A sufficient excess of potassium permanganate must be added at the beginning to preserve the pink color throughout the period of standing; otherwise a brown precipitate of manganese dioxide always forms. With 10 c.c. of aqueous eugenol—the amount always used in the titrations in this work—30 c.c. of potassium permanganate is the minimum starting amount.

2. Twenty-four hours' standing is sufficient and is approximately the minimum.

3. Attempts to hasten the reaction by heating produced irregularities in the quantity of permanganate that was used.

The quantity of oil in 1 c.c. of an aqueous solution was calculated from a determination of the c.c. of permanganate reduced by a known weight of the oil. About two drops was weighed upon a small watch glass which was placed in a large beaker. Some sulphuric acid and an excess of the potassium permanganate were added. The solution was allowed to stand for three days, with occasional stirring. The titration was then finished by the method already given. The results could be duplicated approximately. At the time of finishing the titrations some of the beakers had the odor of the oils. The assumptions must be made that the permanganate oxidized the oils as completely when added to the oil drops as when added to the filtered aqueous solution, and that the oil as a whole, and not certain constituents, dissolved to form the aqueous solutions. It seems likely that any errors from the above causes would be approximately the same for each oil, hence the results obtained in the experiments would be comparable.

MATERIALS AND REAGENTS.

Metal Surfaces. Square pieces of remelted commercial rolled lead were used, having an area on each side of 4 sq. cm. and a thickness of 0.3 mm. After being used, the squares were remelted, rerolled and recut as before. Fresh squares were used, thus avoiding the danger of changing the nature of the surface and so affecting the adsorption by an acid treatment. Before being used, the squares were rolled into cylindrical form around a stirring rod, to prevent them from adhering to each other and so lowering the total surface exposed to the solution.

Zinc, copper, tin, cadmium and silver squares were cut from sheet metal. Enough were on hand to make cleaning of used squares unnecessary.

Powdered antimony had to be used, the brittle nature of the metal preventing the use of squares as with the other metals. The lump metal was ground in a mortar and those particles were taken which passed through a 30- but not through a 40-mesh sieve. The microscope showed these particles to be in general like long cones or like broken cylinders or pyramids. The antimony particles had an average width of 0.1 mm., but an average length of nearly 0.6 mm. The surface area of an average antimony particle was considered as being greater than that of a cone of like dimensions but less than that of a cylinder. Under these assumptions, the area was calculated to be 0.65 sq. mm. The relation of weight to area was determined by weighing a counted number of the particles. A weight of antimony having an area equal to the metal squares used in the other experiments was employed each time.

Aqueous Solutions of the Oils. These solutions were made as follows: Ten c.c. of the essential oil were shaken in the shaking machine with a liter of distilled water for an hour and then allowed to stand 24 hours before being used. These solutions were always filtered just before using. The solutions gradually lost strength, due, perhaps, to oxidation of the oil, a yellow solid material separating out. The eugenol, which was used in the majority of the experiments, was especially purified as follows: The volatile oils mixed with the eugenol were removed by distillation with steam from an alkaline solution, the sodium eugenate being non-volatile. The pure eugenol was then distilled with

steam after sulphuric acid had been added to break up the eugenate. A pale yellow oil was obtained which gradually became brown upon standing. The other essential oils were not purified.

Apparatus: The flask containing the metal squares and the aqueous oil was shaken continuously but gently in a shaking machine, which was operated by a water motor. The shaking was necessary in order to obtain equilibrium in a reasonable time.

Procedure: Into a 100 c.c. flask, clean and dry, the aqueous solution of the oil and the squares were introduced. The number of squares varied, but 20, having an area of 160 sq. cm., was the usual number; 25 c.c. of oil solution were generally used. The flask was then stoppered, placed in the shaker and gently shaken for the desired time. The liquid was passed through a filter, the first portions being discarded. Ten c.c. of the filtrate were then titrated as already described. Experiments showed that appreciable amounts of the oil were not adsorbed by the filter paper.

PRELIMINARY EXPERIMENTS.

A number of experiments with eugenol and lead were made to determine the best conditions for the tests as regards number of squares, volume of solution and time of shaking. The conditions thus determined were assumed to apply to the other oils and metals. These experiments showed that 20 squares of lead shaken for 3 hours in 25 c.c. of the solution gave satisfactory results. The bulk of the adsorption takes place in the first hour and at the end of the third hour equilibrium has been approximately reached. This was shown by ten experiments which were stopped after different intervals of time:

Time of Shaking.	Total Adsorption in Terms of cc. N/10 $KMnO_4$.
15 min.	16.8
30 min.	20.2
45 min.	22.8
1 hour	23.9
2 hours	25.3
3 hours	28.9
4 hours	29.1
8 hours	29.1
12 hours	29.2
24 hours	29.3

The Effect of Some Acids and Salts on Adsorption.

The substances used were introduced into the shaking flasks 5 minutes before the 3-hour shaking period was over. The result, using 160 sq. cm. of lead surface, 25 c.c. of eugenol solution and 5 of the acid or salt solution, was:

Substance Added.	Total Adsorption in Terms of N/10 $KMnO_4$.
Blank	27.9
Water	26.1
Nitric acid*	28.4
5 percent lead acetate	12.2
Sulphuric acid*	7.2
Perchloric acid*	6.0
Acetic acid*	5.5
Hydrochloric acid*	2.5

* Dilute acid of ordinary laboratory strength.

It is likely that the nitric acid oxidized some of the eugenol, hence the apparently increased adsorption.

The acids or salts may have been adsorbed with consequent reduction in the quantity of adsorbed eugenol. Another explanation is that the acids decomposed the lead eugenate with liberation of the eugenol. This would assume that there was a chemical combination between the lead and the eugenol, whereas all of the data indicate adsorption. The addition of 5 c.c. of water lessened the adsorption, due simply to the dilution of the solution whereby the equilibrium was shifted. This slight reduction would be produced in all the cases by the dilution with the acid or salt solution.

Re-adsorption of the Eugenol into the Water Phase.

If the lead containing the adsorbed eugenol is shaken a number of times with fresh portions of water, the eugenol is approximately all liberated and re-adsorbed into the water phase. The eugenol is given up much more quickly if the lead with the adsorbed eugenol is treated with portions of dilute acid. This is to be expected from the action of the acids in lessening the adsorption, as was shown in a previous section. In each experiment, 20 squares of lead, having an area of 160 sq. cm., were shaken for three hours in 25 c.c. of eugenol solution. These

squares were then transferred to a clean dry flask with 25 c.c. of fresh water or dilute acid solution and shaken for 15 minutes. This process was repeated, using fresh solution each time, as long as any eugenol was returned into the fresh solution.

Solution to Readsorb the Eugenol	Eugenol in the lead at the beginning: in terms of N/10 $KMnO_4$.	Amount of Eugenol returned to each 25 cc. Portion of Solution in each period of 15 min. shaking													Eugenol not returned
		1	2	3	4	5	6	7	8	9	10	11	12	13	
Water . . .	31.	12.8	4.8	3.1	3.	2.3	1.3	1.2	0.5	0.4	1.0	0.7	0.3	0.	0.2
Sulphuric* . .	29 6	15.6	7.9	2.	2.3	1.1	0.6	0.	0.	0.	.....	.....	.....	.....	0.1
Perchloric* .	29.9	19.1	1.2	2.4	3.	2.7	1.3	0.1	0.	0.	.....	.....	.....	.....	0.1
Acetic* . . .	30.4	19.	6.1	3.9	1.	0.3	0.	0.	.....	.....	.....	.....	.....	.....	0.1
Hydrochloric*	30.5	24.2	3.	1.1	1.	0.8	0.	0.	.....	.....	.....	.....	.....	.....	0.4

* These acids consisted of 5 c.c. of the dilute acids (as used in the laboratory) and 20 c.c. of water.

The results show that with water alone, twelve successive treatments of the lead squares are necessary, with a nearly equal return in the second to the tenth treatment, whereas with the hydrochloric acid nearly all is returned in the first shaking. It should be noted that acetic acid is not much different in its action from perchloric acid, whereas in electrolytic lead baths the eugenol effectively restrains crystalline structure only in the perchlorate bath.

In another experiment, eight successive shaking periods of three hours each in pure water were necessary for the return of all of the eugenol. This was a total of 24 hours as compared with three hours where 12 periods of 15 minutes each were used. This shows that most of the re-adsorption into the water takes place quickly.

Efforts to Obtain Complete Adsorption.

The eugenol could not be completely adsorbed from a solution. Eugenol, equivalent to 120 c.c. of permanganate, was shaken 3 hours with 20 lead squares (160 sq. cm. area). These lead squares were removed and fresh ones added. This was repeated until there was no further adsorption. The quantity of eugenol adsorbed during the periods of shaking was 43.5, 47.0, 8.7, 3.0,

0.1 and 0. This shows an unadsorbable residue of 17.7 c.c., or 14.7 percent. The eugenol adsorbed by each set of squares was returned to water at about the same rate, thus showing no apparent difference between the first and the last eugenol to be adsorbed. Similar experiments with the other oils were not tried.

Adsorption of the Returned Eugenol.

Experiments showed that the eugenol which had been returned to water from the lead squares could be adsorbed again by lead squares. The eugenol could be again returned to water by shaking with portions of fresh water and could be again adsorbed by lead. These successive adsorptions and returns were repeated four times. No change in the properties of the eugenol could be detected from the data except that all of the eugenol re-adsorbed into the water phase could be adsorbed by fresh lead squares.

Adsorption of Several Oils by a Number of the Common Metals.

These experiments were carried out as already described. The data are given on the following page.

The data under *a* seem to show that the total quantity of oil adsorbed is not as important as the specific nature of the oil itself. Eugenol (clove oil) is the best addition agent in lead perchlorate baths and promotes good deposits in lead fluosilicate baths. The quantity of eugenol, by weight, adsorbed by lead and by the other metals is much less than that of some of the other oils, which are very much inferior as addition agents.

In studying these data it must be remembered that the aqueous oil solutions were of different concentrations as regards the milligrams of oil in 1 c.c., hence in the cases of high adsorption the solutions were more concentrated. For this reason, the data under *b* and *c* are perhaps better for generalizations. The proportion or percent of the oil taken from the solution is a good measure of the adsorbing power of the metals, especially where the actual weight concentrations of the various aqueous oil solutions varied.

The data under *b* and *c* are so nearly alike that the same comparisons and deductions hold for both, but differ from those for *a*. The arrangement of the oils in the order of decreasing ad-

Adsorption per 160 sq. cm. of metal surface from 25 c.c. of aqueous solution in 3 hours. *a*, in milligrams; *b*, in terms of N/10 $KMnO_4$; *c*, percent of total oil in the solution which was adsorbed.

Name of Oil	Lead			Antimony			Copper			Cadmium			Zinc			Iron			Tin			Silver		
	a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*
Eugenol	14.7	52.5	36	13.5	48.1	33	10.0	35.8	25	8.9	32.0	22	8.9	31.7	22	7.3	26.2	18	4.5	16.2	11	3.8	13.7	9
Bay	22.1	47.0	33	22.0	46.9	33	15.6	33.1	24	14.6	31.1	22	13.9	29.7	21	11.8	25.2	18	7.2	15.3	11	6.0	12.8	9
Bergamot	44.1	40.1	28	52.2	47.5	34	32.0	29.1	21	28.0	25.5	18	25.5	23.2	17	21.0	19.1	14	16.6	15.1	11	13.0	11.8	8
Citronella	42.0	38.2	28	46.5	42.3	31	32.2	29.3	21	28.9	26.3	19	23.9	21.7	16	19.4	17.6	13	16.2	14.7	11	13.3	12.1	9
Cumol	59.0	34.7	23	85.5	56.2	37	29.2	17.2	11	17.3	10.2	7	18.0	10.6	7	29.0	17.1	11	9.0	5.3	4	5.3	3.1	2
Pineneedle	31.1	33.8	32	33.0	35.9	34	18.5	20.1	19	16.4	17.8	17	10.9	11.8	11	18.6	20.2	19	11.2	12.2	12	4.2	4.6	4
Fennel	16.0	30.8	26	15.3	29.5	24	14.2	27.3	22	10.6	20.3	17	14.1	27.1	22	5.3	10.3	9	5.0	9.7	8	2.2	4.2	3
Peppermint	40.1	27.1	25	45.4	30.7	28	31.4	21.2	19	34.5	23.3	21	37.0	25.0	23	13.9	9.4	9	12.7	8.6	8	7.5	5.1	5
Carvol	15.5	21.2	19	8.8	12.1	11	14.8	20.3	18	15.8	21.6	19	10.1	13.8	12	5.0	6.8	6	3.1	4.3	4	1.2	1.6	1
Thymol	17.2	21.2	21	3.7	4.6	4	8.9	11.0	11	7.8	8.4	8	8.6	10.6	10	5.8	7.2	7	1.0	1.2	1	0.9	1.1	1
Red Thyme	22.6	18.8	18	5.5	4.6	4	13.0	10.8	10	9.5	7.9	8	12.2	10.2	10	8.4	7.0	7	1.2	1.0	1	1.0	0.8	1

sorption from data in *b* and *c* differs widely from the order depending upon the weights of oils adsorbed from data under *a*.

Experiments[1] have shown that the oils arranged in the order of their effectiveness in the lead perchlorate bath are: eugenol (clove oil), bay, citronella, peppermint, bergamot, fennel, pine-needle and thymol. This order agrees with the order under *b*, except for peppermint, which comes seventh. Experiments[2] with antimony fluoride baths showed that clove oil is much more active than thymol. This agrees with this table. Experiments have not been tried with these oils as addition agents in copper baths. Clove oil[3] did not give good results with cadmium. Other oils were not tried. The oils have very little effect upon zinc deposits from sulphate baths[4], upon tin[5] from various baths, and still less upon silver.[6] Clove oil in a ferrous sulphate bath[7] gave a fair deposit.

Antimony is much more sensitive to addition agents than any other metal that has been tried. Its position seems to be wrong; it should rank before lead.

Eugenol, which is the most effective oil in plating baths, is adsorbed in greater percentage than any other oil; this is as it should be.

An objection to these experiments is that the condition in neutral aqueous solutions are very different from those in electrolytic baths containing salts and free acids. The acids and salts influenced the adsorption very much in the case of lead and eugenol. Hydrochloric acid decreased the adsorption most of all. This agrees with the experimental fact that no addition agent is appreciably effective in a chloride bath. Acetic acid ranks next, then hydrochloric and then sulphuric. Lead chloride or sulphate baths cannot be used because of the slight solubility of these salts. Good deposits can be obtained from lead perchlorate and eugenol. Lead acetate and eugenol do not give good deposits.

[1] Mathers and Overman, Trans. Am. Electrochem. Soc., **21**, 313 (1912).
[2] Mathers, Means and Richards, Trans. Am. Electrochem. Soc., **31** (1917).
[3] Mathers and Marble, Trans. Am. Electrochem. Soc., **25**, 319 (1914).
[4] Watts and Shape, Trans. Am. Electrochem. Soc., **25**, 292 (1914), and unpublished work in this laboratory.
[5] Mathers and Cockrum, Trans. Am. Electrochem. Soc., **26**, 133 (1914).
[6] Mathers and Kuebler, Trans. Am. Electrochem. Soc., **29**, 417 (1916).
[7] Watts and Li, Trans. Am. Electrochem. Soc., **25**, 532 (1914).

It seems unlikely that the small difference between the adsorption of eugenol in the presence of perchloric acid and of acetic acid can account for the great difference in the behavior of lead perchlorate and lead acetate baths.

ERRORS.

1. Essential oils are mixtures. It is possible that the constituents which are of most importance as addition agents are not reducing, hence the permanganate consumed may not be a measure of the thing desired. The oil adsorbed, as given in the tables, includes only those constituents of the oils that reduce permanganate under the conditions of the titration. The weight of oil oxidized by 1 c.c. of permanganate varied, being 1.48 milligrams for peppermint, but only 0.28 for eugenol. The odor of peppermint was still noticeable after an excess of permanganate had been present for three deays. This shows that part of the constituents of the peppermint are not oxidizable under the conditions of the experiment. The same thing was true for some of the other oils.

2. The variation in concentration of the aqueous solutions of the various oils introduced an error in the tables. The greater the concentration, the larger the quantity adsorbed in milligrams (*a*) and in terms of N/10 permanganate (*b*) and the lower the percent adsorbed (*c*). The concentration of the aqueous oil solutions was as follows:

Name of Oil.	Milligrams in 1 c.c. of aqueous solution.	Milligrams of oil oxidized by 1 c.c. of N/10 $KMnO_4$
Eugenol	0.764	0.28
Carvol	1.087	0.73
Pineneedle	0.92	0.92
Bay	1.17	0.47
Citronella	1.18	1.1
Fennel	0.63	0.52
Peppermint	1.28	1.48
Bergamot	2.2	1.1
Thymol	0.77	0.81
Red Thyme	2.2	1.2
Clove	...	0.36
Cumol	3.18	1.7

3. These solutions were much more concentrated in addition agent than most plating baths.

4. Neutral and salt-free solutions were employed, whereby the known differences in action produced by the different acid ions were neglected.

5. If any of the oils contained large percentages of unabsorbable reducing material (eugenol contained 14.7 percent) a serious error would be introduced. The adsorption of the adsorbable constituent might be very complete, whereas the analysis might indicate a small adsorption.

6. It seems unlikely that any error is present in the calculation of the area of the antimony particles used in an experiment. The difference in the nature of the surface of the crushed antimony particles from that of the rolled surface of the other metals may have introduced an error. However, some experiments with granulated lead (test lead) particles did not show any difference from rolled lead squares.

SUMMARY.

Every metal used adsorbed every oil to a certain extent, hence the mere adsorption of an oil by a metal proves nothing concerning the value of the oil as an addition agent.

The more readily an oil is adsorbed the greater its effect as an addition agent.

The arrangement of the oils in the order of decreasing adsorption is nearly the same for many of the metals and a similarity exists in the cases of the others.

The metals arranged in respect to decreasing adsorption of the oils are: lead, antimony, copper, cadmium, zinc, iron, tin and silver. An arrangement of these metals as regards increasing difficulty in preventing rough crystalline deposits by the use of addition agents would agree in most cases with this order. Copper should probably come first and antimony second. However, no research has been made of addition agents in copper baths.

These conclusions only hold in a general way. Tin and silver adsorb the oils, but are influenced very little by these oils in

plating baths. Antimony adsorbs thymol in smaller quantity than tin or silver adsorb certain other oils, yet antimony is very much affected by thymol.

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DISCUSSION.

F. C. ATWOOD[1]: I wonder if the authors have followed any definite scheme in adding the essential oils, or tried to prove any definite theory that would aid the general subject of electro-plating. There seems to be no reason why an addition agent should be of value in plating baths in general because it is found of value in any given one. The fact that so small an amount of addition agent is necessary to give marked effects in a plating bath suggests a very interesting theory. If we study colloidal solutions of metals, so-called sols, we find that addition agents of certain kinds prevent precipitation of the metal. Such addition agents are called protective colloids. For gold sols, protective colloids can be arranged in a series which gives a convenient expression of their protecting power. My idea is that if we were to arrange another series of colloids which showed their value as addition agents in gold-plating solutions, the two series would be closely parallel. Might it not be possible to study the protective effect of various colloids on sols of silver, copper, etc., at the same time that their effect is being studied in plating baths. In this way, we might arrive at some definite conclusions as to the action of addition agents. We could also predict whether a colloid would make a good addition agent in electro-plating by simply studying its protective effect on a sol of the metal in question.

G. B. HOGABOOM[2]: These are addition agents not used in electro-plating. The addition agents in sulphur solutions and cyanide

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[2] Research Laboratory, Scovill Mfg. Co., Waterbury, Conn.

solutions have not been studied much; we do not know of any outside of carbon bisulphide, which is an old one. The pieces which Dr. Mathers has submitted as samples would hardly answer the purpose of general silver plating. Silver plating methods are peculiar, in that the deposit must not be too dense when it has to be burnished. If the deposit is too dense, then it will not give under the burnishing and will not flow, as it is commonly termed; whereas, these deposits are so dense that they would refuse to flow, and, therefore, whatever defects there are in the base metals could not be covered. It would not be a commercial process for electro-plating.

I wonder if Dr. Mathers has tried to nickel-plate any of the tin deposits. There is a great deal of trouble at the present time in trying to nickel-plate on tin so as to make it adhere. At the banquet of the Electro-platers' Society in New York City, the subject was brought up and discussed by Prof. Smith's assistant, Dr. Lukens, of the University of Pennsylvania, and he brought out the fact that tin being dimorphous, if you deposited it at one temperature it would not adhere, and if it is deposited at another temperature it would adhere. I was wondering whether the deposit of tin from fluo-silicate would be affected in the same way.

F. C. MATHERS: I have never tried any nickel-plating on tin.

A. D. COWPERTHWAITE[3]: Answering Mr. Hogaboom's question, regarding nickel-plating on tin, I have not tried nickel-plating on sheet tin, but on tin-plated steel, and I have not noticed any difficulty about the nickel adhering. I simply nickel-plated from a heated nickel solution, and while I have never turned out any large quantities of this work, the work being done in an experimental way, it seemed to be very satisfactory as far as I could see. The plate was bright and adhered as well as it did on copper.

G. B. HOGABOOM: That sustains Dr. Lukens' argument, that adherent plating of nickel upon tin should be done in a heated solution; that it cannot be done in a cold solution.

O. P. WATTS[4]: I would suggest that the better adherence of the nickel in this case is because nickel deposited from a hot solu-

[3] Chemical Engineer, The Edmunds & Jones Corp., Detroit.
[4] Asst. Professor of Applied Electrochemistry, University of Wisconsin.

tion is softer and has less tendency to flake than when deposited from a cold solution.

F. C. MATHERS: We have had in mind a number of these experiments concerning the metals in a colloidal condition, but our time was taken up with this and other work, and we did not get an opportunity to try them. Such experiments are difficult, and I did not want to begin them until I had a fairly clear idea of just how to carry them through.

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 5, 1917, President FitzGerald in the Chair.

ADDITION AGENTS IN THE ELECTRODEPOSITION OF SILVER FROM UNCOMMON SILVER SALTS.

By F. C. Mathers and T. G. Blue.

[*Abstract.*]

Silver perchlorate, fluosilicate, fluoride and ethylsulphate baths were electrolyzed with glue, peptone, gum arabic and various other addition agents. The deposits were somewhat better than with the same addition agents in nitrate baths.

Phenolsulphonic acid, cresolsulphonic acid, and their sodium or ammonium salts, sodium naphthalenesulphonate and sodium benzene sulphonate, 3 percent in each case, when added to the silver baths, including the nitrate, restrained the formation of crystals in the same way as tartaric acid, but less effectively.

The use of unusual salts of silver does not seem to offer possibilities of obtaining much better deposits than from the nitrate.

Experiments already published[1] show that glue, peptone, clove oil, aloin, gum arabic and other similar addition agents, which have been successfully employed in restraining the crystalline structure of other electrodeposited metals, are of little value in the electrodeposition of silver from silver nitrate baths. In that research, three percent of tartaric acid in the baths was found to give solid, smooth silver cathodes.

This research gives the results with the various addition agents in silver salts of the less common acids such as hydrofluoric, fluosilicic, perchloric and ethylsulphuric. An addition agent may have little effect with one salt of a metal while it will give a good deposit with another salt of the same metal, hence it was thought that smooth cathodes might be obtained with some of these silver salts

[1] Mathers and Kuebler, Trans. Am. Electrochem. Soc. (1916), 29, 417.

and the ordinary addition agents. In general, the deposits were crystalline or spongy, hence only a very brief description of the experiments will be given. The baths contained 3 percent of silver and about 3 percent of the free acid and were electrolyzed at 0.8 amp. per sq. dec. (7.2 amp. per sq. ft.).

Fluosilicate and fluoride baths gave about the same results, although the cathodes from the fluosilicate baths were slightly smoother and less crystalline. Both baths were somewhat reduced by the organic addition agents. The addition of 0.04 to 0.06 percent of glue, with further additions of 0.02 percent every 12 hours, gave hard, smooth deposits except for short rough projections on the edges. It was not found possible to continuously maintain the proper quantity of glue. The decomposition of the baths or an excess of glue caused the deposits to become spongy. Peptone was not as good as the glue. Gum arabic had practically no effect.

Perchlorate baths, with 0.02 percent of glue or peptone, gave deposits with peculiar wavy striations. The cathodes were firm and fairly smooth on the edges. Good conditions could not be maintained, hence thick deposits could not be prepared. Thicker deposits could be prepared than from the fluoride or the fluosilicate. Gum arabic, 0.1 percent, restrained the crystallization but the deposits were rough and striated. Clove oil, tragacanth, digitalis, phloridizin, mucic acid and pyrogallol made the deposits less crystalline, but thick deposits could not be prepared in any case. Alcohol, small amounts of potassium cyanide, albumen, and casein showed no apparent effect. The deposits were crystalline from baths containing 50 percent of alcohol or glycerine; the further addition of 1 cc. of carbon disulphide, clove oil or carbon tetrachloride did not stop the crystalline structure but 0.02 percent of phthallic acid gave glossy, smooth deposits except for long, slender crystals on the edges.

The ethylsulphate baths were not as good in any case as the ones already described.

Tartaric acid in these baths gave solid, firm but somewhat rougher deposits than it did in the nitrate baths.[1] Ammonium phenolsulphonate, phenolsulphonic acid, cresolsulphonic acid, sodium benzolsulphonate and sodium naphthalenesulphonate (3

[1] *Vide ante.*

percent) in any of the baths, including the nitrate, had about the same effect as tartaric acid but the deposits were not as smooth and maintenance of the baths in good working conditions was more difficult. In the nitrate baths, the nitric acid acted upon the organic substance in most cases. It seems likely that some of these sulpho acids could be used in place of the tartaric acid in the nitrate baths, if there were any commercial demand for solid, non-crystalline silver deposits. Any theory accounting for the action of addition agents must explain the effects of these sulpho acids in the silver baths. Oxalic or succinic acid, 0.02 percent, partially restrained the formation of crystals.

The authors wish to thank the American Electrochemical Society and its Committee on Assisted Research for the loan of the silver which was used in this investigation.

Indiana University,
Bloomington.

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TESTS OF ANTIMONY PLATING BATHS.

By F. C. Mathers and K. S. Means.

[*Abstract.*]

Deposition of antimony from numerous electrolytes was tried, such as the tartrate, chloride, oxalate, and fluoride, with the addition of glue, peptone, aloin, etc., as addition agents. The most satisfactory bath is the fluoride, containing free hydrofluoric acid and a small amount of aloin, resorcinol, alpha-naphthol, beta-naphthol, or salicylic acid.

Introduction:—The object of this work was to perfect or devise a satisfactory bath for the electro-deposition of antimony. The preliminary work required the testing of the baths that have been recommended for the electro-deposition of antimony. The various antimony baths were prepared and electrolyzed according to the directions given. In general the results were unsatisfactory, except in the case of the fluoride bath, which is described more completely in another paper.[1] Sulphide baths were not tried.

Manipulation:—A cathode of sheet copper having a total area of 50 sq. cm. (7.6 sq. in.) was suspended between two anodes of cast antimony in a 225 c.c. beaker, containing 200 c.c. of the solution being tested. Paraffin vessels were used with the fluoride baths. In oxalate baths, the anodes were suspended by lead strips and in the other baths by platinum wires. The anodes were placed in cloth bags to keep slime and other solid material from reaching the cathodes and producing roughness. The baths were gently stirred by air bubbles.

[1] Trans. Am. Electrochem. Soc. (1917), **31**, 293.

Tartrate Baths:—Complex antimony tartrates in aqueous solution do not hydrolyze, with precipitation of basic antimony salts. It is this property that has led to their use in plating baths.

The baths tried were:

	Grams of Tartar Emetic in 100 c.c. of Solution.	Grams of Tartaric Acid in 100 c.c. of Solution.	Other Substances per 100 c.c. of Solution.
I	130	130	65 cc. conc. HCl.
II	8	8	3 g. $(NH)_4Cl$.
III	6	4	.....
IV	6	4	6 g. Rochelle Salts

The first bath gave a bright, smooth deposit which could be made of good thickness. Only a very small current could be used. Higher currents gave black deposits. This bath is very concentrated, hence expensive to prepare. The other baths gave dark deposits and the voltages were high. These experiments showed that the tartrate baths were unsatisfactory.

Chloride Baths:—The baths tried contained from 3 to 3.5 grams of $SbCl_3$ and from 9 to 60 c.c. of conc. HCl in 100 c.c. of solution. The deposits were crystalline and rapidly became rough as the thickness increased. The presence of the strong HCl is necessary to prevent the hydrolysis of the $SbCl_3$, with the precipitation of antimony hydroxide.

Oxalate Baths:—The double salt of antimony oxalate with potassium or ammonium oxalate is soluble in water and does not hydrolyze. It seemed to the authors of this paper that good deposits might be expected from this bath because good deposits had been obtained from the corresponding stannous ammonium oxalate bath.[2]

Baths containing from 3 to 14 percent ammonium oxalate, from 2.7 to 4 percent antimony trichloride and from 0.4 to 7 percent of oxalic or acetic acid were tried. The best deposit, which was finely crystalline and smooth, was obtained from a bath containing 8 percent ammonium oxalate, 2.7 percent antimony chloride and 1.3 percent oxalic acid. Owing to deterioration of the bath, the deposits became rough after a few days and

[2] Mathers and Cockrum, Trans. Am. Electrochem. Soc. (1916), **29**, 411.

finally non-adherent. This trouble was due, at least in part, to poor corrosion of the anode, which gassed after becoming covered with a white, hard coating. Gum arabic, glue, peptone, aloin, tannic acid or beta-naphthol, 0.02 to 0.05 percent, made the deposits less crystalline and more smooth. The deposit with gum arabic was best. The essential oils also improved the deposits, which became harder and smoother. A long list of addition agents, including formin, sucrose, levulose, dextrose, alcohol, turpentine, urea, catechin, gum benzoes, licorice and phloridizin, in quantities of 0.05 percent, did not improve the deposits.

Experiments with the oxalates were abandoned because the rapid deterioration of the baths showed that they were worthless for extended use.

Fluoride:—Antimony fluoride, free hydrofluoric acid, and any one of a number of organic addition agents as aloin, resorcinol, alpha-naphthol, beta-naphthol or salicylic acid gave entirely satisfactory deposits. This bath is recommended as much the best for antimony plating.

Indiana University,
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A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 5, 1917, President FitzGerald in the Chair.

ELECTRO-DEPOSITION OF ANTIMONY FROM FLUORIDE BATHS CONTAINING ADDITION AGENTS

By F. C. Mathers, K. S. Means and B. F. Richard.

[*Abstract.*]

The deposition of antimony is studied from fluoride baths containing free hydrofluoric acid, with the addition of various kinds of organic addition agents. Without additions the deposit is crystalline, while very small amounts of various addition agents make it smooth and glossy. Aloin and clove oil are found most effective additions; the correct very small quantity must be maintained in the bath. The current efficiency is close to 100 percent.

INTRODUCTION.

Antimony fluoride is readily soluble in water, does not hydrolyze and, being entirely inorganic, does not decompose prejudicially or become altered during electrolysis. No other antimony salt possesses these properties which are so essential in making a plating bath.

These experiments with the fluoride baths are largely a story of the use of addition agents to make the deposits less crystalline and more smooth.

MANIPULATION.

The baths contained 5 grams of antimony as fluoride and 3 grams of free hydrofluoric acid in each 100 c.c. and were made by dissolving 60 grams of commercial antimony oxide in 114 grams of 48 percent commercial hydrofluoric acid and diluting to 1,000 c.c. (8 oz. antimony oxide and 15.3 oz. hydrofluoric acid per gallon). The volume of each experimental bath was 200 c.c. The baths were electrolyzed for about three days before begin-

ning the tests, because rough striated deposits were always produced for this length of time. It was supposed that this was due to impurities in the antimony oxide. A bath made from pure antimony trichloride and hydrofluoric acid did not give this rough deposit in the beginning.

A current of 0.8 amp. per sq. dec. (7.4 amp. per sq. ft.) was used. The deposits were less smooth with 1 amp. and, with still higher currents, they became rougher especially when thick cathodes were being made. The voltage was 0.65 with the cathode midway between the two anodes, which were 4 to 5 cm. apart. The total area of each cathode was 50 sq. cm. (7.7 sq. in.) and the area of the anodes, on the faces towards the cathode, was 30 sq. cm. (4.6 sq. in.).

Thick deposits were prepared whenever possible because this gave the surest way of judging the value of the bath. Many baths might do passably well for thin deposits, but only a really good bath will give a good thick deposit. Many of the deposits were 0.5 to 1 cm. in thickness.

Solutions of the addition agents in water or in alcohol, if they were insoluble in water, were prepared of a known strength, usually 3 grams in 100 c.c. New portions of the addition agents were added every 12 hours, hence the percent of addition agent, as used in the following description, means the grams which were added each 12 hours for each 100 c.c. of bath.

The solutions were gently stirred by air bubbles which entered each bath through a piece of rubber tubing. The anodes, suspended by platinum wires, were in cloth bags, to prevent anode slime from reaching the cathodes where it produced rough places. The anodes dissolved readily during the electrolysis.

EXPERIMENTAL.

With No Addition Agent:—The deposit from a bath containing no addition agent was crystalline. Many of the crystals, increasing in size more rapidly than others, formed pointed projections, some of which, on the edges of the cathode, finally produced short circuits. A thick deposit was very rough, but the crystals were solid and coherent and were no more brittle than ordinary cast antimony.

Adding Essential Oils:—The essential oils were so active that it was impossible to uniformly maintain the proper quantity in the baths. Any excess caused the deposits to crack, while a deficiency did not restrain the formation of the crystals. In every case the deposits were somewhat rough.

Oil of eucalyptus, which was the least active as shown by the greater quantity which could be added without causing the deposits to crack, gave a finely crystalline, fairly smooth deposit when 0.0025 c.c. per 100 c.c. of bath was added. When 0.005 c.c. was added, the deposit cracked badly.

Clove oil, which was much more active, gave rougher deposits, and 0.0012 c.c. produced cracking in some cases.

The oils showed a tendency to give a dark-colored, polished appearance to the cathodes, especially in the presence of other addition agents. Any essential oil with glue or peptone gave a very glossy, dark deposit. Oxalic acid, which by itself produced no beneficial action, prevented an oil, as clove oil, 0.0025 c.c., or thymol, or any of the others, from cracking the deposit, hence a fairly good cathode was obtained.

Phenols:—Resorcinol (0.025 percent twice daily) gave one of the best deposits that was obtained during the work. The cathode was finely crystalline, grey in color and very smooth.

Alpha-naphthol or beta-naphthol (0.025 percent twice daily) gave deposits that were as good as those with the resorcinol except for some nodules or bumps. The cathodes were very finely crystalline.

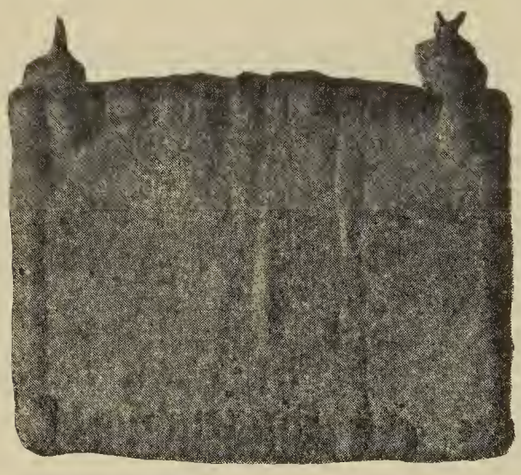
Phenol (0.06 percent twice daily) gave a more crystalline deposit which showed a tendency towards roughness on the edges.

It should be noted that the simple phenol was less active than the more complex compounds.

Picric acid (0.015 to 0.07 percent twice daily) had no beneficial effect. The baths soon became dark in color and the deposits spongy.

Vegetable Extracts:—Aloin (0.025 percent twice daily) gave a deposit which was the equal of any obtained during this work. The simultaneous addition of 0.0025 c.c. of clove oil per 100 c.c. of bath (one drop of a solution of 1 part of clove oil in 10 parts of alcohol) made the deposit smoother, more glossy and of a

darker color. This quantity of clove oil was used up in 6 or 7 hours, as was shown by the appearance of the cathode changing from glossy and lustrous to a grey. This particular deposit was the smoothest and perhaps the best of any.



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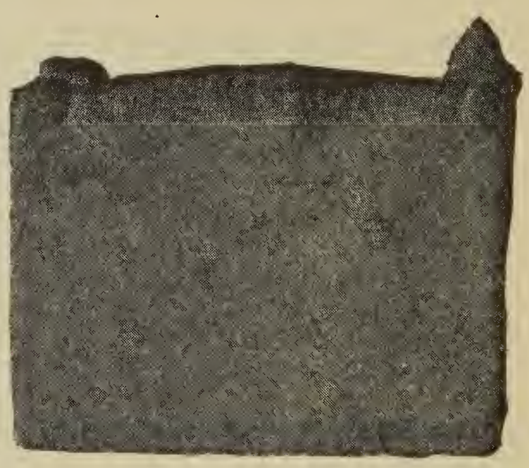

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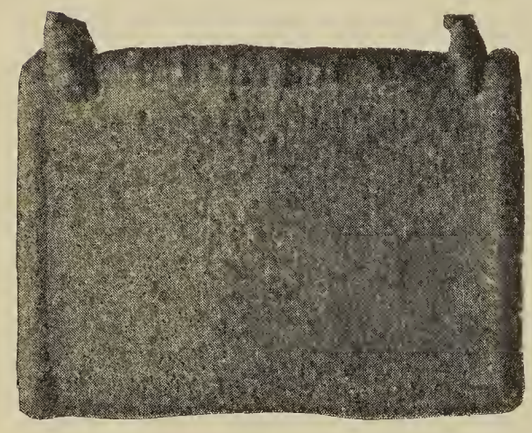

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The baths, from which these cathodes were deposited contained, per 100 c.c., 5 gms. of antimony as the fluoride, 3 gms. of free hydrofluoric acid and addition agents as follows:

1. 0.025 gms. aloin and 0.0025 c.c. of clove oil, twice daily.
2. 0.025 gms. resorcinol, twice daily.
3. 0.025 gms. alphanaphthol, twice daily.
4. No addition agent. (Note the roughness.)

The current density was 0.8 amp. per sq. dec.

Tannic acid (0.0015 to 0.015 percent twice daily) gave a striated dark deposit with the smaller quantity and a spongy deposit with the larger quantity, after electrolysis for several days.

Aromatic Acids:—Salicylic acid (0.015 percent twice daily) gave an excellent, smooth, glossy deposit. A smaller quantity of addition agent would perhaps have been better, as this cathode had some small cracks or checks.

Benzoic acid (0.015 percent twice daily) gave a deposit which was free from projections, but small spherical nodules were plentiful on the surface.

Phthalic acid (0.0015 percent twice daily) gave a fairly good deposit which had some smooth projections on the edges. Phthalic acid was very active, hence larger quantities caused the deposits to crack.

Alkaloids:—The alkaloids, quinine, strychnine and morphine, gave smooth deposits which, however, were somewhat too thick or heavy on the edges. In each case, 0.015 percent of the hydrochloride was added twice daily. This amount was in excess of the quantity required in the case of the strychnine bath, which continued to give a good deposit for many days after the addition of strychnine was discontinued.

The morphine gave the best deposit, as shown by the greater smoothness of the edges.

Glue, Peptone and Gum Arabic:—Experiments with glue are always interesting because glue is the addition agent that is best known. In this case, as in many others, glue is inferior to other substances.

Glue (0.025 percent twice daily) gave a peculiarly striated deposit which showed a tendency towards projections on the edges. The deposit was distinctly crystalline. Larger amounts of glue (0.05 percent twice daily) made the deposit smoother, and after this quantity had been added for a number of days, the deposit became very dark and glossy, with a tendency towards cracking. Still larger quantities of glue (0.075 percent twice daily) gave a deposit which showed no indication of crystalline structure. There was also less roughness on the edges, but it was very glossy and brittle and showed cracks. The longer the bath was run the more glossy was the deposit. This seemed to indicate accumulation of glue in the bath, but with a new cathode and the addition of no more glue the deposit became grey in color and finely crystalline in 72 hours. Glue possesses one great advantage over many of the other addition agents in that an excess is less harmful in causing the deposits to crack from the starting sheets. The simultaneous addition of very small amounts of an essential oil (0.0006

c.c. of clove oil per 100 c.c. of bath) made the deposits very much more glossy.

Peptone, an animal product chemically somewhat similar to glue (0.015 percent twice daily), gave a fairly good deposit which was grey and finely crystalline but somewhat rough on the edges. Peptone was more active than glue, as shown by badly cracked deposits which were produced by 0.022 percent of peptone twice daily. In no case was a glossy deposit produced.

Gum arabic (0.03 percent twice daily) gave slightly striated deposits which were free from cracks but were rough on the edges. A larger amount of the gum arabic (0.045 percent) made the deposit smoother and somewhat glossy.

Alipathic Acids:—Oxalic, succinic or tartaric acid, in quantities as large as 0.12 percent twice daily, were of very little effect. The deposits were practically as crystalline and as rough as when no addition agent was added. Clove oil (0.0025 c.c. per 100 c.c. of bath) in combination with either of these acids made the deposits fairly smooth but somewhat cracked. This quantity of clove oil in the absence of another addition agent would have produced bad cracking.

Sugars:—Sucrose, glucose, or levulose (0.5 percent twice daily) were practically without effect.

Miscellaneous:—Urea, formin, alcohol, and acetone were practically without effect. Carbon disulphide and hydrogen sulphide made the deposits somewhat less crystalline and more smooth.

CURRENT EFFICIENCY.

The cathode efficiency, determined daily for 6 days, averaged 100.68 percent in a 200 c.c. bath to which 0.05 grams of beta-naphthol was added twice daily and 100.38 percent in a bath to which 0.05 gram of aloin was added twice daily. The high values are probably due to the inclusion of electrolyte. Any oxidation of the surface of the deposit or the absorption of the entire quantity or addition agent would be negligible in cases like these where thick deposits weighing about 9 g. were obtained in each run.

The anode efficiencies could not be accurately determined, due to the loss of slime which was produced by impurities.

PROPERTIES OF THE DEPOSITED ANTIMONY.

Specific Gravity:—The specific gravities of samples from the beta-naphthol bath were 6.68, 6.6 and 6.64 as determined in a specific gravity bottle against water at 20°. Cast antimony has a density of 6.7.

Brittleness:—The deposits, when struck, break perpendicularly to the starting sheet. The broken pieces show a structure in this direction resembling the grain in a split piece of fine-grained wood.

SUMMARY OF ACTION OF ADDITION AGENTS.

Antimony in a fluoride bath is very much more sensitive towards addition agents than any metal that has been tested in this laboratory. This is shown by the many different classes of addition agents that are effective and the unusually small amount of each substance which is required. It is almost certain that all the other substances in the classes which were beneficial would have acted, more or less successfully, as addition agents. The testing of all the individual substances was thought unnecessary. There may be new classes of beneficial addition agents which the authors have overlooked.

It seems that antimony is the best metal to use in testing out theories of addition agents because it is the most sensitive.

It was not the intention of this work to test any theory, but a few relations which were found should be pointed out.

Almost equally good deposits were obtained with phenols (resorcinol, alpha-naphthol or beta-naphthol), with vegetable extracts (aloin), and with alkaloids (morphine) and with aromatic acids (salicylic or benzoic). Glue, peptone and gum arabic were less satisfactory. The essential oils were exceptionally active, but were unsatisfactory very largely for this reason.

Some classes of substances as sugars, alipathic acids, alcohols, etc., were of no value.

As regards the essential radical in the addition agents, it seems that the aromatic hydroxyl or carboxyl group is the necessary factor. Substances containing either of these groups have acid properties and also the property of forming compounds with metallic salts. Salicylic acid containing both the hydroxyl and the

carboxyl was more active than benzoic. Phthalic acid with its two carboxyl groups was more active than benzoic. Resorcinol with its two hydroxyl groups was more active than phenol. The naphthols were more active than phenol, a deportment that must be explained by the greater activity of the heavier aromatic radical. The alkaloids and essential oils in many cases contain the hydroxyl group. It seems that the formation of a complex between the addition agent and the antimony fluoride might be necessary for the beneficial action of an addition agent. Examples are given in the literature of compounds between metallic salts and the classes of addition agents that were found to be successful.

SUMMARY.

Antimony fluoride and free hydrofluoric acid give the best bath for the electro-deposition of antimony. The bath that was used contained 5 percent of antimony as the fluoride and 3 percent of free hydrofluoric acid. A suitable organic addition agent must be used to prevent a crystalline structure. These baths work easily and without any indication of deterioration or undesirable change, if the proper quantity of addition agent is maintained and if the ordinary precautions in plating are observed.

Without the organic addition agents the deposits are rough and crystalline. The smoothest, thickest, least crystalline deposits were obtained by adding aloin, beta-naphthol, alpha-naphthol or resorcinol. The addition agent, 0.025 percent, must be added every 12 hours during the electrolysis.

The deposits are grey and finely crystalline except that too large a quantity of some of the addition agents makes the deposits darker and more glossy. This result can also be produced by adding very small amounts of clove oil (0.0012 c.c.) along with any of the other addition agents. The deposits are brittle, like ordinary cast antimony, hence if a plated article is bent the deposit will crack.

Aloin is the cheapest of the satisfactory addition agents. If the deposit becomes dark or shiny in color or tends to crack, less addition agent must be used. A crystalline rough structure indicates the need of more addition agent.

Excess of almost any of the addition agents causes the deposits

to crack. Essential oils, as clove, thymol, etc., were so powerful that it was impossible to maintain the correct quantity in the baths.

Glue is helpful, but it gives only a fair deposit as compared with aloin.

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DISCUSSION.

W. C. BROOKS[1]: I would like to know the strength of the thin plating. Does it peel, and does it have any tensile strength?

F. C. MATHERS: If the material on which it is plated is subjected to bending, the deposit will crack, because it is brittle.

W. C. BROOKS: Will it stand much use?

F. C. MATHERS: Not very much. The deposit is brittle, like ordinary antimony. If you have a thin film of antimony it will break. It would be possible to make it so thin that the cracking would be very serious, and it would not stand very much use.

O. P. WATTS[2]: Do you use the method of extracting the aloes with water or alcohol?

F. C. MATHERS: I extract with water. The usual thing, where a little of it is used, is to make a strong solution, a definitely known quantity of which is added twice daily. There is no trouble in handling it.

C. G. FINK[3]: All work in connection with metallic antimony ought to be encouraged on account of the backward state of the art in this country. We have big competitors in Asia. Every set of experiments that tends to bring about or eventually lead to the cheapening of the process of extracting antimony from its ores, is valuable on that account.

In regard to the addition of aloes, why add a little every twelve hours? Why not add it continuously? Is there any difficulty in so doing?

[1] Chemical Engineer, National Carbon Co., Cleveland.
[2] Asst. Professor of Applied Electrochemistry, University of Wisconsin.
[3] Research Chemist, Edison Lamp Works, Harrison, N. J.

F. C. MATHERS: There would be no difficulty, but we seem to get satisfactory results by adding it at these intervals. It would have been better if it had been added continuously.

J. W. RICHARDS[4]: I agree with Dr. Fink that probably the chief use of this information may be in the electrolytic refining of antimony, and just as in the electrolytic refining of lead and silver the use of these addition agents has become general, so in the electrolytic refining of antimony it may materially assist in solving some difficult questions.

I should like very much to hear from any platers present, as to whether antimony has any advantages in plating; I do not know of any.

G. B. HOGABOOM[5]: We do not know of any value of antimony as a plating metal. I understand, however, that it will act on some materials as a resistant to tarnish, but as Dr. Mathers brought out, it is so brittle that it could not be handled without breaking, and it would not be possible for platers to make use of it.

F. C. FRARY[6]: I was reliably informed some years ago that all of the so-called platinum plating on analytical weights made in Germany was not platinum plating, but antimony plating.

F. C. MATHERS: The baths work very easily. There is no deterioration, and no difficulty in keeping the bath in good operation over long periods of time.

[4] Professor of Metallurgy, Lehigh University.
[5] Research Laboratory, Scovill Manufacturing Co., Waterbury, Conn.
[6] Research Chemist, Oldbury Electrochemical Co., Niagara Falls, N. Y.

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 5, 1917, President FitzGerald in the Chair.

THE EVOLUTION OF HYDROGEN FROM CYANIDE PLATING SOLUTIONS.

By Oliver P. Watts and Albert Brann.

[*Abstract*]

Experiments were made with silver and copper cyanide solutions, with the addition of varying amounts of free potassium cyanide, to determine the effect of the latter in producing liberation of hydrogen at the cathode. The effect is much greater with copper solutions than with silver solutions. Test experiments show that the liberation of hydrogen is direct, and not due to action of the free cyanide, but to raising of the single potential necessary to deposit the metal until it reaches that sufficient to electrolytically set free hydrogen.

The deposition of copper and brass from the cyanide solutions used in plating is accompanied by an evolution of hydrogen, which becomes greater as the amount of free cyanide is increased. In explanation of this it cannot be said that deposition of metal from cyanide solutions is always associated with the liberation of hydrogen, for in silver plating no hydrogen is evolved. Such evolution of hydrogen means that the efficiency of deposition of metal diminishes with increase of the free cyanide.

In seeking an explanation of this phenomenon, at least two possibilities must be considered. The first involves the well-known solvent power of cyanide solutions for many metals, and would explain the lowering of the current efficiency with increase of free cyanide as due to a solvent action of the electrolyte on the deposit. The second possibility is that the hydrogen does not come from reaction between the metal and cyanide, but that it is directly deposited by the current instead of a chemically equivalent amount of metal.

When it is considered that the addition of a very moderate proportion of potassium cyanide can entirely prevent the deposition of copper, even when high current densities are employed, the first supposition appears unlikely to be the correct explanation. This view is still further confirmed by a recent experiment with a nickel-plating solution. This was divided into two parts, to one of which one percent by volume of concentrated sulphuric acid was added; the two solutions were then electrolyzed in series for a half hour at 0.3 ampere per square decimeter, with nickel anodes and copper cathodes. The cathode in the original solution gained 0.021 gram, an efficiency of 85 percent, but that in the acid electrolyte did not show a trace of nickel, and had not increased in weight. To determine whether the hydrogen that appeared in place of nickel in the latter solution was deposited directly by the current, or came from the dissolving of nickel by the acid as fast as deposited, the nickel-plated cathode was hung in the acidified solution for a half hour. It lost only 0.0026 gram in weight. The lowering of the current efficiency of nickel baths which results from the addition of strong acids is due to the plating out of hydrogen in place of nickel, and not to attack of the deposit by the acid.

Although it was deemed certain that the same condition would be found true for the copper cyanide solution, a confirmatory test was made. Equal volumes of the laboratory copper-plating bath were taken, to one portion 30 grams per liter of sodium cyanide was added, and the two electrolyzed at 0.15 ampere for 30 minutes. The cathodes gained 0.1518 and 0.0295 gram, efficiencies of 87.3 and 17 percent. On allowing the cathodes to stand in their respective electrolytes for a half hour with no current passing, the former lost 0.0016 and the latter 0.040 gram. The low current efficiency of cyanide copper solutions containing much free cyanide is due to the direct deposition of hydrogen instead of copper, and not to corrosion of the cathode by cyanide.

It is recognized that in electrolysis of solutions containing two or more metals, deposition by the electric current acts selectively; there is a tendency to deposit first that metal whose potential is lowest, and only when the greater part or all of this has been deposited, is the metal next lowest in potential deposited. It is this selective action which has made possible the electrolytic

refining of metals. Although the fundamental principle is as stated, its practical operation is not so simple as indicated above; for unless there is a considerable difference of potential between the metals a complete separation does not take place, but there is a simultaneous deposition of both metals. Even when the potentials are quite different a few cases are known in which both metals are found in the deposit, as when electrolyzing the sulphates of zinc and iron. Current density and the relative concentrations of the metals in the electrolyte are important factors.

It is in this tendency to deposit only the element of lower potential when the difference of potential is great, and for both to be deposited together when there is a small difference of potential, that we must look for an explanation of the peculiarities in regard to the evolution of hydrogen in cyanide plating baths.

First it will be well to review the facts. In a solution of the double cyanide of copper and potassium containing no free cyanide, Field[1] obtained a current efficiency of 97.6 percent; but in commercial plating baths it is necessary to have some free cyanide present in order to secure good anode corrosion, and consequently the current efficiency is reduced to 70 to 80 percent, and there is always a considerable evolution of hydrogen. Not only is there no hydrogen evolved from the standard silver-plating solution, but much free cyanide may be added without causing gas to be given off at normal current densities. By raising the current density to such a point that metal cannot be supplied at the cathode by diffusion as fast as needed, hydrogen must be deposited from either solution, even if no free cyanide be present.

Caspari[2] gives 0.23 volt as the overvoltage of hydrogen on copper in normal sulphuric acid, *i. e.*, a copper cathode must have a potential 0.23 volt higher than a cathode of platinum before hydrogen will be deposited on it. This corresponds to —0.13 volt for the discharge potential of hydrogen on copper. Since the potential of copper, —0.51 (normal calomel electrode = —0.56 volt) is 0.38 volt below the discharge potential of hydrogen, it is easy to see why there is no deposition of this gas when a copper sulphate solution is electrolyzed at any reasonable current density. Copper and hydrogen are so far apart in potential that only copper is deposited.

[1] The Principles of Electrodeposition, p. 189.
[2] Z. phys. Chem., 1889, 30, 89.

In normal potassium cyanide copper may show a potential as great as 0.8 volt, and, if the discharge potential of hydrogen on copper is the same in this as in copper sulphate solution, hydrogen should be deposited more readily than copper, and the low current efficiency of copper solutions containing a large excess of potassium cyanide is readily understood.

To determine the effect of variations in concentration of cyanide on the single potential of the metal and on the discharge potential of hydrogen, measurements were carried out in four solutions made by dissolving 65, 32.5, 6.5, 0.65 grams of C. P. potassium cyanide per liter, *i. e.*, in approximately normal, half, tenth, and hundredth normal solutions. The results are given in Table I, in which the discharge potential was taken as the lowest potential at which gas escaped steadily from the cathode. Since potentials vary with the amount of air dissolved in the electrolyte, with the time, current density, etc., and because the instruments employed were not of the highest accuracy, the numerical values given should be regarded as approximations only; yet it is thought that they are sufficiently accurate to permit the drawing of certain general conclusions. All potentials are positive unless marked otherwise.

TABLE I.

Single Potential Measurements in KCN Solution.

Concentration of KCN Added	N/100	N/10	N/2	N/1
Silver:				
Single potential	0.04	0.18	0.28	0.31
Discharge potential of H	.59	.56	.62	.55
Difference	.55	.38	.34	.14
Copper:				
Single potential	.53	.67	.78	.82
Discharge potential of H	.67	.70	..	..
Difference	.14	.03	..	..
Brass:				
Single potential	.53	.67	.77	.80
Discharge potential of H	.55	.70	..	..
Difference	.02	.03	..	..
Iron:				
Single potential	—0.13	—0.10	—0.04	..
Discharge potential of H	.56	.59	.59	.64
Difference	.69	.69	.63	..

It is seen that the potentials of all the metals rise as the concentration of cyanide is increased, although with iron the change

is so small as to be negligible in practical work. Allowing for the errors previously referred to, it appears that the discharge potential of hydrogen on the metals tested is independent of the strength of solution within the limits tested. The magnitude of the differences between the potential of the cathode metal and the discharge potential of hydrogen should be a measure of the difficulty of depositing this gas along with the metal in plating.

No values are given for the discharge potential of hydrogen on copper and brass in normal and half normal potassium cyanide, because gas was evolved on merely immersing these materials in the solutions; this would seem to show that the discharge potential of hydrogen is less than the potential of the metals in these solutions. The data of the table indicate that a very high current density would be required to deposit hydrogen from a silver-plating bath containing little free cyanide, that the current density required for this will become less as the amount of free cyanide is increased, and that in copper and brass baths gassing should occur at low current densities, even with the least amount of free cyanide that it is practicable to use.

Solutions of the double cyanides of the strength usually used for plating with silver and copper, but without free cyanide, were prepared by boiling an excess of the freshly precipitated metallic cyanide in a solution of potassium cyanide, and filtering. The potentials of silver and copper were measured, each in its own solution, without and with the addition of various amounts of free cyanide. The results appear in Table II.

TABLE II.

Potentials of Silver and Copper in their Double Cyanides.

Grams of Free Cyanide per Liter.	0	10	20	40	60
Silver in $KAg(CN)_2$.....	—0.62	—0.10	—0.06	—0.01	0.02
Copper in $KCu(CN)_2$.....	—0.27	...	0.55	0.69	0.73

A larger amount of potassium cyanide appears to be necessary to produce the same elevation of potential in the presence of the double cyanide of the metal than in its absence; this indicates that the deposition of hydrogen from plating solutions will be less easy than was deduced from the measurements of Table I in potassium cyanide alone.

The above experiments were undertaken to furnish an explanation for the observed deposition of hydrogen from cyanide copper and brass baths, and its failure to appear in silver plating. The following conclusions may be drawn:

1. The great lowering of the current efficiency of copper and brass plating solutions caused by the addition of considerable amounts of sodium or potassium cyanide is due to elevation of the potential of the metal that is being deposited, until it equals, and finally exceeds, the discharge potential of hydrogen, so that this gas is deposited instead of metal, according to the long-known selective action at the cathode in electrodeposition.

2. The solvent action of cyanide on the deposit is comparatively unimportant.

3. The failure of the addition of free cyanide to the silver bath to produce the marked lowering of efficiency observed in copper and brass solutions, is due to the fact that the rise of potential of silver with increase of free cyanide is less marked than for copper and brass. Even 60 grams of free cyanide per liter leaves the potential of silver considerably below the discharge potential of hydrogen, instead of above this, as is the case for brass and copper.

Laboratory of Applied Electrochemistry,
University of Wisconsin.

DISCUSSION.

F. C. FRARY[1]: In regard to the potentials of silver in the double cyanides, at the San Francisco meeting of this Society, in 1915, Mr. Porter and I presented a paper[2] showing that the effect of free cyanide on the potential of silver was a function, not of the absolute quantity of free cyanide at all, but of the ratio of the free cyanide to the double cyanide. It seems to be, therefore, peculiarly unfortunate that on page 303 Dr. Watts did not specify the strength of the solution of double cyanide he used,

[1] Research Chemist, Oldbury Electrochemical Co., Niagara Falls.
[2] Trans. Am. Electrochemical Society (1915), 28, 307.

as I am sure no one else would know what strength was used. I hope the information may be corrected in the discussion, and also if possible, that the vacant space in Table II, column 2, will be filled with the proper value, as that is the most interesting and important one of all, since it corresponds approximately with the free cyanide normally used in the plating bath, and it is in that part of the curve that the most rapid change of direction takes place, as is shown by both Dr. Watts' figures and our own.

With regard to the third conclusion, I would point out as a more apparent reason, from Dr. Watts' own figures, for the hydrogen being evolved in the copper bath and not in the silver bath, that in the silver bath you have 0.55 volt difference of potential between the metal and hydrogen, and in the copper bath only 0.14 volt. It is much easier to raise the cathode potential to 0.14 volt above the single potential of hydrogen than to raise it 0.55, and I suggest that this is more probably the principal factor in the case than the slightly different rate of increase of the copper potential with the addition of cyanide.

A. D. COWPERTHWAITE[3]: Is it not possible for the addition of cyanide to prevent the ionization of the double copper salt? That might explain the failure to deposit when the amount of free cyanide reached a certain point.

O. P. WATTS: I am not prepared to enter into a discussion of the ionization, but prefer to leave that to someone who is better acquainted with the ionization theory than I.

F. C. FRARY: As far as silver is concerned, the silver ion concentration calculated from our measurements in n/4 silver potassium cyanide solution is about 8×10^{-12}, while in the same solution containing also free cyanide to the extent of n/40, it is only 4×10^{-18}, or about one two-millionth as much as it was without free cyanide. Whether you believe the figures or not depends on how much trust you put in the formulae we have for the calculation of ionic concentration from electrode potentials.

O. P. WATTS: Since my remarks on page 303 had reference, as is perfectly clear, to all plating baths, Prof. Frary can hardly regard it as "peculiarly unfortunate" that the composition of

[3] Chemical Engineer, The Edmunds & Jones Corp., Detroit.

these is omitted. The two solutions of Table II, page 307, contained, as made up initially, 46 grams of $KAg(CN)_2$ and 30.7 grams of $KCu(CN)_2$, respectively, per liter.

Perhaps the third conclusion will be less liable to be misunderstood if the following addition be made to it: If the potential of a metal is below the discharge potential of hydrogen upon it, as with silver, no hydrogen is electrolytically liberated, but if the potential of the metal exceeds the discharge potential of hydrogen upon it, as is the case with brass and copper in cyanide plating solutions containing the usual amount of free cyanide, hydrogen will be deposited.

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 5, 1917, President FitzGerald in the Chair.

AUTOMOBILE STORAGE BATTERIES.

By W. C. Brooks.

[*Abstract.*]

The chemistry of the lead accumulator is reviewed; the service required in automobiles is classified as for ignition, starting and lighting, and motive power. The construction and design of each kind is discussed, also their electrical characteristics, followed by description of the causes of trouble and failure.

INTRODUCTION.

Following the invention of the pasted-plate type of lead storage battery in 1880 by Faure in France and Brush in America, there has been no rival to this form of accumulator in portable service where high capacity per unit weight is desired. It was therefore natural for this form of accumulator to develop into the present-day automobile storage battery. It has only one competitor, the nickel-iron cell which, due to its high initial cost, internal resistance, and comparative bulkiness is at present restricted to certain classes of industrial truck service. The nickel-iron cell is not used at all, to the writer's knowledge, in starting service on gasoline cars. No Planté, or electrochemically formed, pure lead plate batteries, which are so familiar in central stations and car lighting service, are used on automobiles, on account of the low capacity per unit weight and the difficulty of making a compact assembly due to expansion of the positive plate in service. The automobile storage battery has, therefore, come to mean some compact, light form of a pasted lead-plate element, generally in hard-rubber jars with thin wood separators. These cells are assembled into a battery with lead-alloy connectors and held in position by a hardwood case or tray.

CHEMISTRY OF THE LEAD ACCUMULATOR.

So much has been written on this subject that no attempt to give any elaborate analysis of the chemical reactions or physical changes within the lead cell will be made. It will be of interest, however, to review briefly some of the chief characteristics of the reaction, as these are the fundamentals upon which the successful operation of the storage battery rests.

The lead storage battery depends upon the following chemical reaction:

$$PbO_2 + Pb + 2H_2SO_4 = 2PbSO_4 + 2H_2O.$$

The reaction has been proven completely reversible.

The left-hand portion of the equation represents the charged condition while that to the right gives the discharged state. The PbO_2 is contained on the positive and the Pb, in a spongy form, on the negative plate, while the H_2SO_4 forms the electrolyte. During discharge the $PbSO_4$ is formed in the surface pores of both plates in a very finely divided condition. The H_2O formed diffuses into and dilutes the electrolyte. This abstraction of SO_4 and addition of H_2O causes the familiar decrease in the specific gravity of the electrolyte, which becomes our most useful means of detecting the state of charge of any lead battery. The discharge voltage of the couple is nominally two volts, though actually somewhat less at most common discharge rates. The charge voltage varies from 2.2 to 2.6 volts, with state of charge and current rate. Open-circuit voltage is about 2 volts at normal temperatures.

The above reaction has almost ideal characteristics, since it is completely reversible, the voltage is comparatively high, and the product of discharge ($PbSO_4$) is so nearly insoluble in the electrolyte that there is little tendency to react when the external circuit is open. Further, the two essential materials, lead and sulphuric acid, are comparatively common substances and easy to obtain in a pure form at reasonable prices. Only one other of the many proposed couples approaches the $PbO_2/H_2SO_4/Pb$ combination in these desirable features. This is the $PbO_2/H_2SO_4/Zn$ couple, which gives a higher discharge voltage, but the zinc tends to dissolve on open circuit and also during the charge, it is deposited in a spongy form on the negative, and falls to the bottom of the

cell. These two faults, due to the high solubility of $ZnSO_4$, spoil what is otherwise a very desirable combination. The Ni/KOH/Fe combination is only partially successful, due to the high price of nickel, high resistance of the nickel oxides, low voltage of the couple, and tendency of KOH to absorb CO_2 from the air.

The $PbO_2/H_2SO_4/Pb$ couple gives a cell with very low resistance. Thus, the voltage is well maintained even when discharged at rates up to 0.52 ampere per square inch (7.75 amperes per sq. dm.) of positive surface. The positive (peroxide) plate is taken as the limiting factor, since there is always an excess of negative capacity. The excess is supplied because experience has shown that extra negative capacity retards the final clogging of the pores with sulphate and thus lengthens its useful life. This does not apply to the positive, since it sheds the surface material continually, though slowly, and presents a clean surface throughout its life under normal conditions.

The maximum rate at which a lead battery can be discharged, with good voltage maintenance, is limited by the rate of acid diffusion between the electrolyte, which acts as a storehouse of acid as well as an electrolyte, and the surface pores of both plates. Also in automobile batteries, the maximum rate is limited by the resistance of the wood separators to acid diffusion and passage of the ions H_2 and SO_4. At normal discharge rates the available capacity of a cell is only a small percentage of the theoretical, due to the difficulty of acid diffusion through the pores of the plate. For this reason, only the surface of the plate reacts at very high rates. The acid penetrates more deeply and gives higher ampere hour capacity as the rate of discharge decreases. This gives the familiar variation of capacity with discharge rate, as shown in Fig. 12.

Obviously, to get higher capacity per unit of plate surface, the diffusion gradient must be steeper. This may be accomplished by using strong acid and an active material of high porosity. Acid strength is limited to about 40 percent H_2SO_4, or 1.300 Sp. Gr., since a higher percentage of acid attacks both plates and separators, especially in hot weather.

It is also clear that to get high capacity per unit volume of cell we must have greatest possible area of plate. Here we are limited by mechanical strength and the necessity of having reserve material.

Charging rates are limited chiefly by gassing, which occurs when the back E. M. F. of the cell, which increases with charging rate, reaches the decomposition voltage of the electrolyte. This occurs at very high rates on a discharged cell, and at any rate on a fully charged cell, due to the lack of $PbSO_4$ ions in the electrolyte. Here, again, we are restricted by the diffusion gradient, as $PbSO_4$ must dissolve, in the pores, before it can become ionized and changed to $H_2SO_4 + Pb$, after which the H_2SO_4 must diffuse through the pores into the more dilute electrolyte. Naturally, at

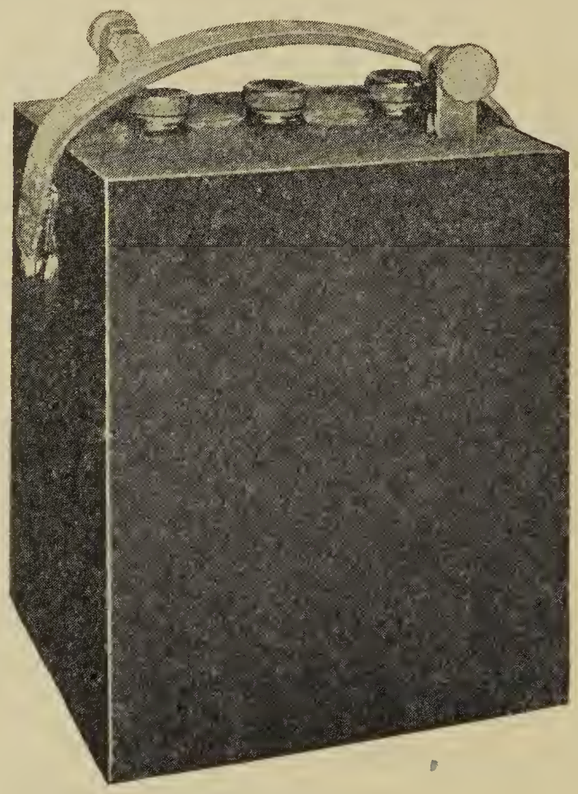


FIG. 1. Ignition Battery.

the end of the charge when most of the $PbSO_4$ is decomposed and the H_2SO_4 formed is dilute and the external electrolyte is strong, there is a very low gradient. So we have the necessarily low finishing rate of charge to prevent excessive gassing. High evolution of gas is undesirable, as the gas bubbles erode the plate surface, the charging energy and water of electrolyte are wasted, and the cell is heated to a dangerous temperature in hot weather. Note, however, that a discharged battery may be charged or boosted at any rate as long as there is no gassing. The ideal characteristic of a charging apparatus is a rate which keeps the voltage just under the gassing point until the last of the charge, when the

rate should be low enough to cause little damage to the cell. This finishing rate is about 0.02 ampere per sq. in. of positive plate (0.31 ampere per sq. dm.). In other words, this rate is low enough to pass through a completely charged cell for several hours without much damage being done.

The foregoing paragraphs review enough of the electrochemistry of the pasted-plate battery to give a basis on which to judge the various factors entering the design and operation of an automobile battery for any variation of service.

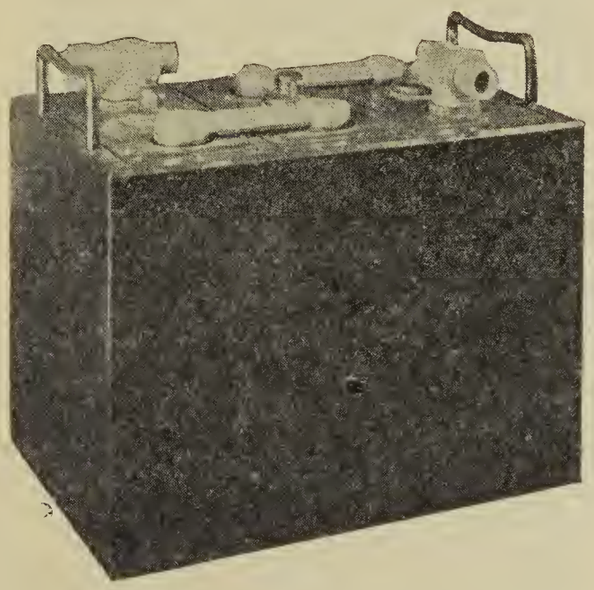


FIG. 2. Starting Battery.

SERVICE.

There are three general divisions of service for automobile batteries: Ignition, starting, motive power.

Ignition.

This service is the first for which storage batteries were applied on gasoline cars. The discharge was extremely low, ¼ to 1 ampere intermittently over a period of a month to a year. The batteries were charged at some service station whenever the customer judged the battery to be exhausted. The storage battery proved fairly satisfactory for such service, but would have been displaced by the dry cell and magneto, had not the development of the high-efficiency tungsten lamps made possible electric lights. Then the storage battery really became the only means to supply continuously the current for both lights and ignition. A few

makers placed a generator on the engine to keep the battery charged; the next development was the cranking motor.

Starting.

The cranking motor and the battery to run it solved the last major problem in popularizing the gasoline automobile. This service demands something entirely different from the battery.

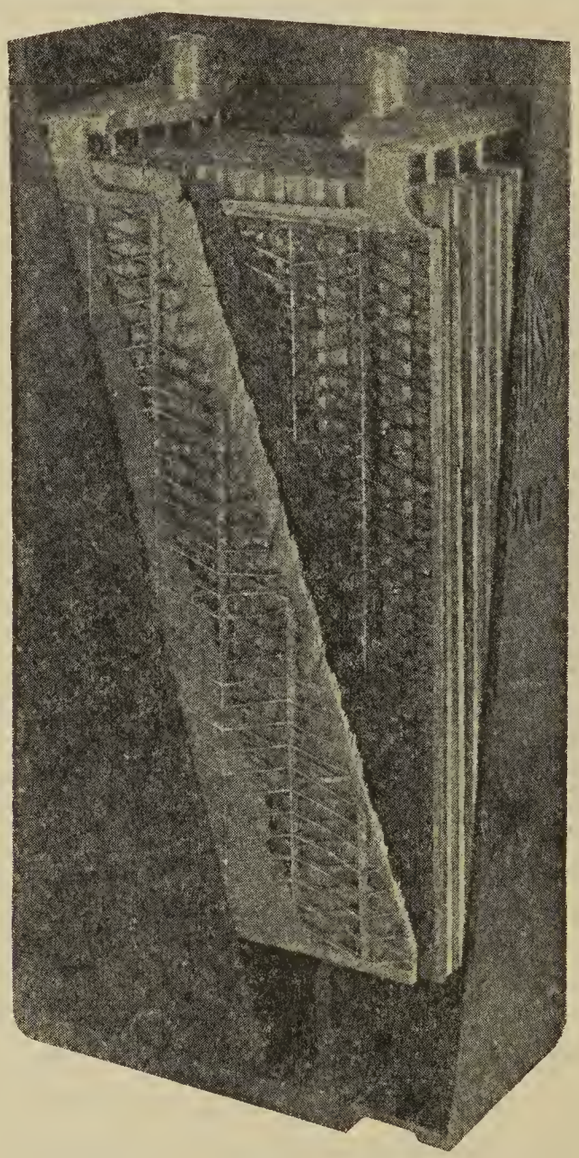


FIG. 3. Pleasure Vehicle Cell.

It not only has to furnish ignition for the engine but current for several lights and energy up to one or two horse power to start the engine. Thus the demand changed abruptly from a fraction of an ampere to several amperes continuously for lights at night, and periodically 100 to 400 amperes for a few seconds or even minutes to crank the motor.

Motive Power.

Electric vehicles were the first to use storage batteries, so it was in this service that the automobile battery has really developed; starting batteries being merely a modification of vehicle battery construction. This service demands for pleasure cars 60 to 80 volts and 25 to 50 amperes for 4 to 6 hours continuous discharge. The discharge is intermittent, generally exhausting the battery about twice a week. Owners frequently recharge before the battery is exhausted. The discharge rate is variable, and batteries are frequently poorly cared for. Electric trucks require 80 to 85 volts and 25 to 400 amperes, depending upon size of truck, grade of road, load and speed. The heaviest current demand is on fire department ladder wagons, but the hardest service is on heavy trucks making long hauls, which exhaust the battery daily.

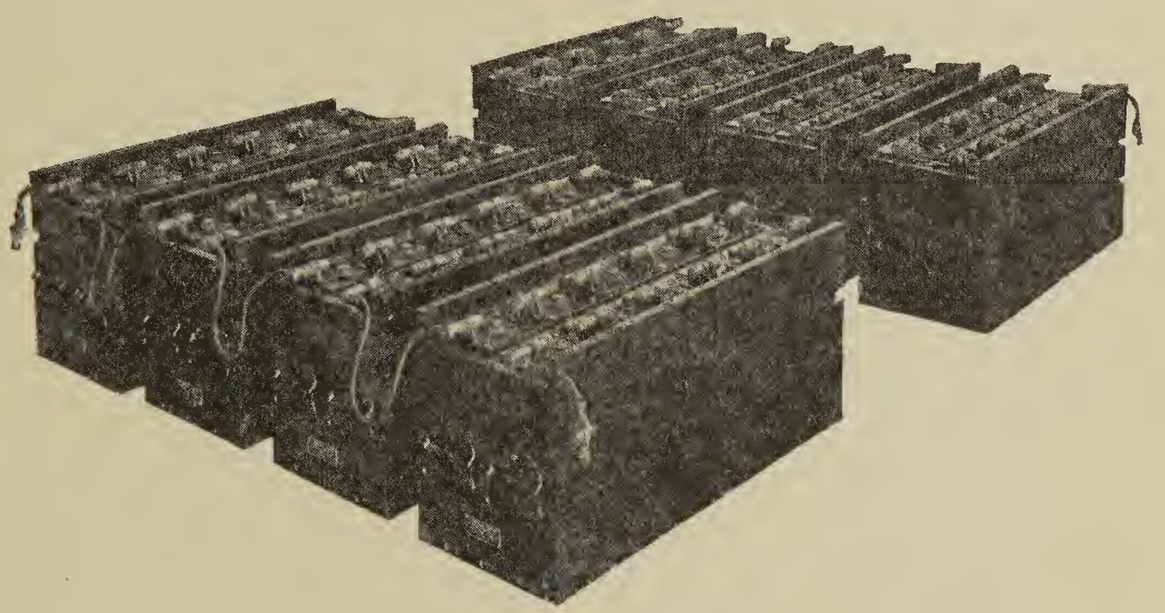


FIG. 4. Truck Battery.

PRODUCTION OF AUTOMOBILE BATTERIES.

Ignition batteries are used for general purposes, such as gas engine ignition, wireless telegraphy, electric toys, railroad signals, dental engines, country house lighting, etc. For automobile service alone the volume of production was never large, probably less than 50,000 batteries per year.

Starting batteries have closely followed, in numbers produced, the automobile production since 1912. Thus in June 30, 1916, there were 2,932,455 cars in use in this country (Automobile, **34**,

1096). Approximately one-third of these were Fords or other cars without electric systems, which leaves about 1,954,000 cars with starting batteries. The average starting battery has to be replaced about every 18 months, so this would show a renewal business of about 1,326,000 batteries per year. In addition there were made in 1916 approximately 1,013,500 cars in this country which had electric systems.

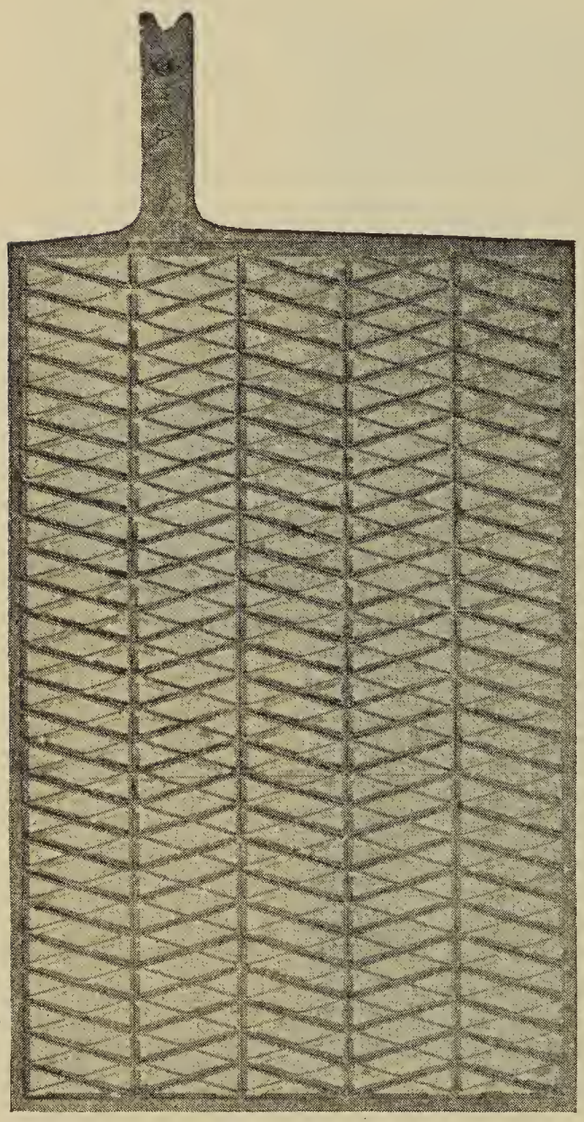


FIG. 5. Herringbone Grid.

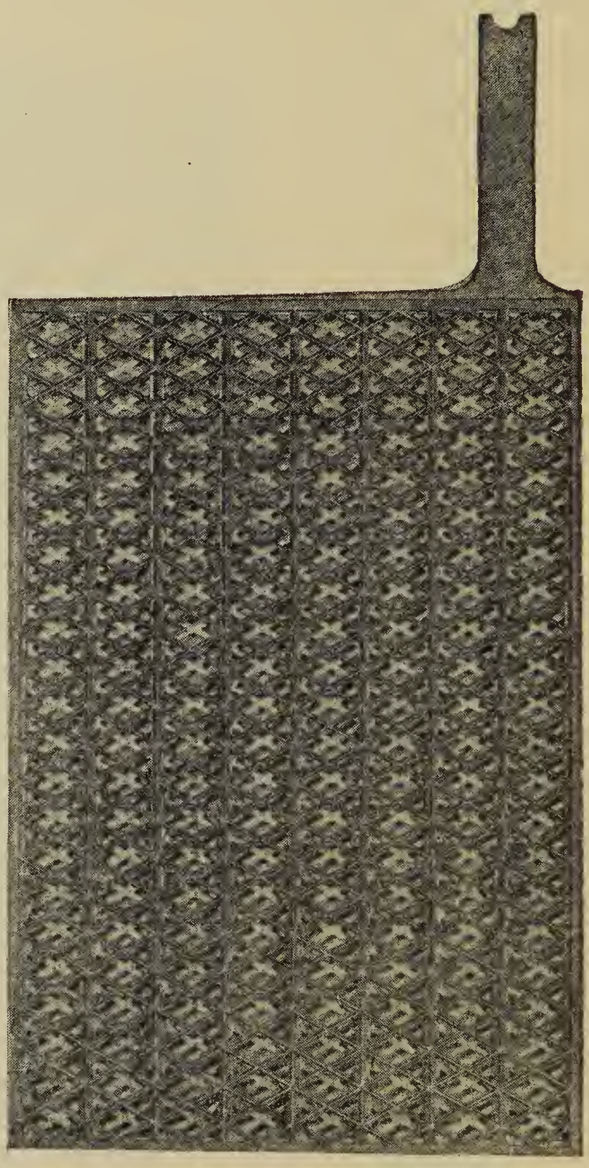


FIG. 6. Diamond Grid.

Motor batteries: Electric vehicles and trucks are produced in much smaller numbers than gas cars, but they require much larger batteries. They also last much longer, with the result that there are several renewals of batteries per car. The total result gave a business to the battery manufacturer in 1915 of approximately 60,000 vehicle batteries. The automobile storage battery is thus

becoming a very important field of electrochemical activity. There is much to improve in the details of manufacture, and careful research together with modern production methods will no doubt make possible even wider application and therefore greater production than has been accomplished in the past.

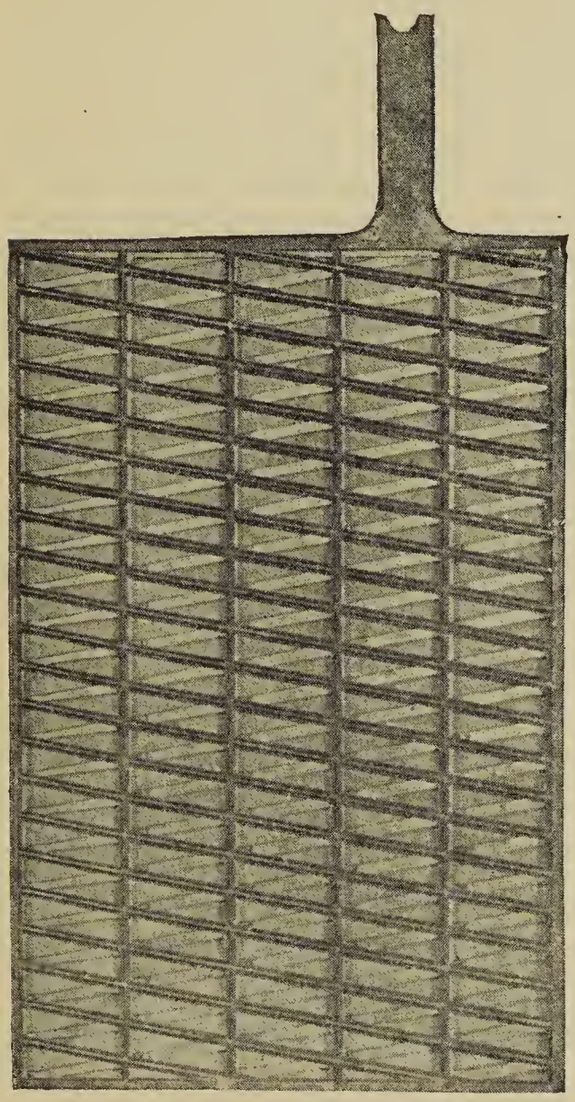


FIG. 7. Staggered Grid.

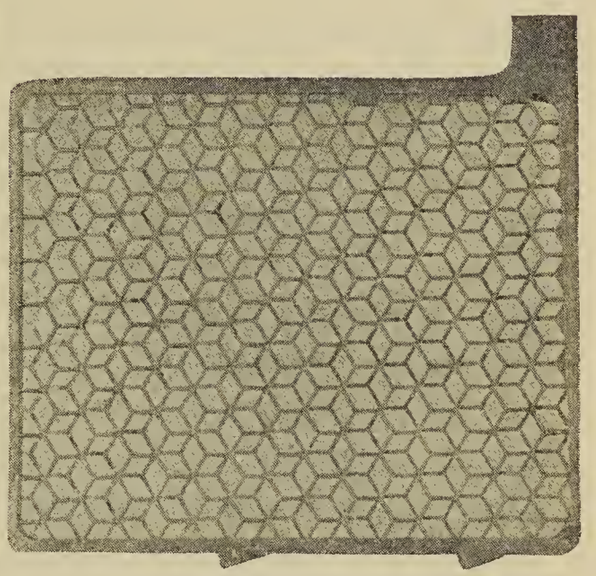


FIG. 8. Hexagon or Honeycomb Grid.

CONSTRUCTION AND DESIGN.

All automobile lead storage batteries are made along the same general lines. The foundation of the battery is the grid, which is cast of antimonial lead containing 5 to 12 percent of antimony. The casting is made by hand pouring of the molten alloy into steel molds. The resulting grid is trimmed and flattened and ready for the application of the active material. Much depends upon the proper design of the grid. It must be stiff, yet somewhat elastic,

be symmetrical so as to expand uniformly, and have its ribs so spaced as to give a maximum conductivity to the plate; yet the size and number of ribs is limited, for the grid must weigh the least amount possible and still have sufficient conductivity and strength.

Some different designs are given in Figs. 5 to 8. They are named in description of their characteristic appearance. Grids and therefore plates vary from 3/32 to 7/32 inch (2.3 to 5.5 mm.) in thickness for automobile batteries. Some forms, such as the hexagon, are not adapted for plates thicker than about ⅛ in. (3.1 mm.) as they would be too heavy, due to the necessity of carrying ribs to the center of the plate. This particular design is the best adapted, of any known to the writer, for thin plates, since it can be made the lightest of all the forms shown for a given cross-section of rib, as it has no heavy vertical ribs. This point is of importance, since a rib less than a millimeter in diameter can become greatly weakened from perforation, thus making the positive plate very brittle and easily broken or buckled. Grids generally should not weigh more than the material which they support.

The active material is made from a mixture of lead oxides and a binding liquid, usually sulphuric acid or ammonium sulphate. The object is to make a mortar or paste which when forced into the grid until it is flush with the surface will harden and form a basis for the formation of true active material.

Much has been claimed for secret processes and mixtures, and many patents have been allowed on such formulas. However, most of these seem to be either harmful or superfluous, since the best plates made are simple mixtures of the right sort of raw materials made under proper and uniform conditions.

The pasted plates are formed by charging them in open tanks of acid having the proper strength, and at such rates as will give the desired structure to the resultant lead peroxide and spongy lead, the charging being stopped in time to leave the correct amount of binding network of large lead sulphate crystals. Here again much depends upon the uniformity of treatment, careful adjustment of current, and strength of acid.

After formation, the plates are dried and stored for use or shipment. The formed and dried plates of the same polarity

are lead-burned to a lead-connector called a plate-strap. This forms a group, and is called a positive or negative group from the plates so connected. One more negative goes into each cell than positive, thus a 13-plate cell is composed of a 6-plate positive and a 7-plate negative group. A positive and negative group, when meshed together and separators inserted, form an element. These elements are slipped into hard-rubber jars 1/16 to 3/16 inch (1.6 to 4.7 mm.) larger than the element, where they rest on ribs which hold them above the bottom of the jar. Starting batteries are so limited for height, and there is so little probability of the sediment becoming very deep, that low ribs are used. Vehicle batteries have ribs 1¾ to 2¾ inches (4.4 to 6.4 cm.) deep. The former will require that the battery be washed out once in a while, and the latter is designed to entirely eliminate this. It does not entirely accomplish the purpose, since very frequently the separators are so soft that new ones are required before a long-lived plate has entirely worn out.

This brings us to a consideration of the separator question. Many kinds have been proposed and used, but the grooved-wood veneer separator has proven superior to all others for automobile battery service. This is because the wood cell-wall, in large numbers, is the only diaphragm found which will allow passage of acid and ions, resist the penetration of loose active material which would short-circuit the cell, and withstand both the vibration of the car and the erosive action of the electrolyte and gas bubbles.

In addition to the wood veneer, hard-rubber sheets 1/64 inch (0.4 mm.) thick and perforated with holes about 0.05 inch (1.3 mm.) in diameter are used next to positive plates in vehicle batteries. This additional separator performs important functions. It keeps the wood away from the peroxide, which tends to soften it, protects the positive plate from erosion of the gas bubbles, and helps to retain the positive material in place. On the other hand, it reduces the active surface of the plate materially, the perforation giving about 30 percent porosity. It is therefore not practical for starting batteries where high rates are demanded.

The hard-rubber jars used to hold elements have been found to be the most economical and satisfactory container, on account of their light weight, resistance to acid, insulating qualities, and small wall thickness necessary for requisite strength. The quality

of the stock may vary largely, and it is this point on which many batteries have failed. The manufacturer, in trying to keep prices down, was content with too low a quality of jar, which became brittle, especially in cold weather, and cracked when a slight strain or blow occurred. This trouble is being very largely eliminated since battery manufacturers began careful testing of jar stock.

Covers are of hard rubber and are sealed in place by a sticky sealing compound of some insulating material.

Vent plugs are necessary to allow escape of gas. They have small holes, which allow the gas to escape but catch the spray of liquid. The plugs fit into holes in the covers which, when the plugs are removed, provide a means of filling the cell with water to replace that lost by evaporation and decomposition.

Cell connectors are lead alloy bars burned to the posts on the plate straps, connecting the positive group of one cell to the negative group of the next one. This leaves two terminal posts on each battery, one on a positive and one on a negative group. These receive whatever kind of connection is used for that type of battery.

After assembly, the battery must receive its initial charge, as the dry plates do not have much capacity. The acid is first allowed to soak into the plates and the charge started at the finishing or gassing rate. This is continued until voltage and specific gravity are approximately constant. The battery is then discharged one or more times until the rated capacity is attained.

Each division of service requires some particular quality which affects construction. Ignition service requires high capacity at long low-rate discharge. The battery must be capable of standing several weeks without losing its charge. Starting batteries also fill the above condition, though thinner plates and more of them per cell will be used. The popular sizes of ignition and lighting batteries are 50, 60, 80 and 100 ampere-hour capacity at one ampere rate, all of these cells each giving 6 volts.

Starting service was originally cranking service, as the thick plate battery was used to turn the engine over slowly, requiring only a moderate discharge from a large heavy high-voltage battery. A year following its introduction voltage dropped to 6, 12 and 18, and the engines were cranked faster. At this time (1913-14), large slow-speed 4-cylinder engines were used, so that

a large battery was required and enormous surge currents were common. Batteries weighing 100 to 150 pounds (45 to 68 kg.) and having 600 to 1,000 watt-hours capacity (at 5 amperes) were common, and the surge current on closing the starting switch often ran to 400 or 500 amperes. This situation was helped materially by developing double-unit systems, using a separate high-speed high-efficiency motor. Then came the high-speed small-volume 6- and 8-cylinder engine, which is easier to start. The result of this development is that now we have as common practice batteries of 360 to 500 watt-hours capacity weighing 40 to 60 lb. (18 to 27 kg.). The voltage problem is being simplified. In 1917 fully 87 percent of the cars will have six-volt systems. The battery is a true starting battery now, too, as it spins the motor over very rapidly (100-150 R. P. M. against former practice of 40-70 R. P. M.), so that a quick start is assured because of the high velocity of gas in the intake pipe of the engine.

The surge current varies on average 6-cylinder cars, at normal temperature, from 120 to 250 amperes, quickly dropping to half that value. In extreme cold weather higher currents occur, and here it is that the true test of a starting battery is made, for the engine is much stiffer to start on account of the cold oil in all the bearings, the gasoline is harder to vaporize, and the battery capacity may be reduced fully half by the low temperature. This variation of capacity with temperature is shown very clearly in Fig. 9. All the above conditions make it imperative to have high sustained voltage at high rates in starting batteries. We have shown that it is necessary to have large plate area for this purpose, and also porous active material, together with a porous separator and strong acid. In addition, all connectors and terminals must be large enough to keep their resistance low.

ELECTRICAL CHARACTERISTICS OF BATTERIES.

Starting Batteries.

We have tested starting batteries from all important manufacturers, very carefully, and give in Table I some of the results of these comparative tests. All the batteries were supposed to have approximately the same rating, and though there is some difference in plate dimensions it is not great, as the column showing positive plate volume indicates.

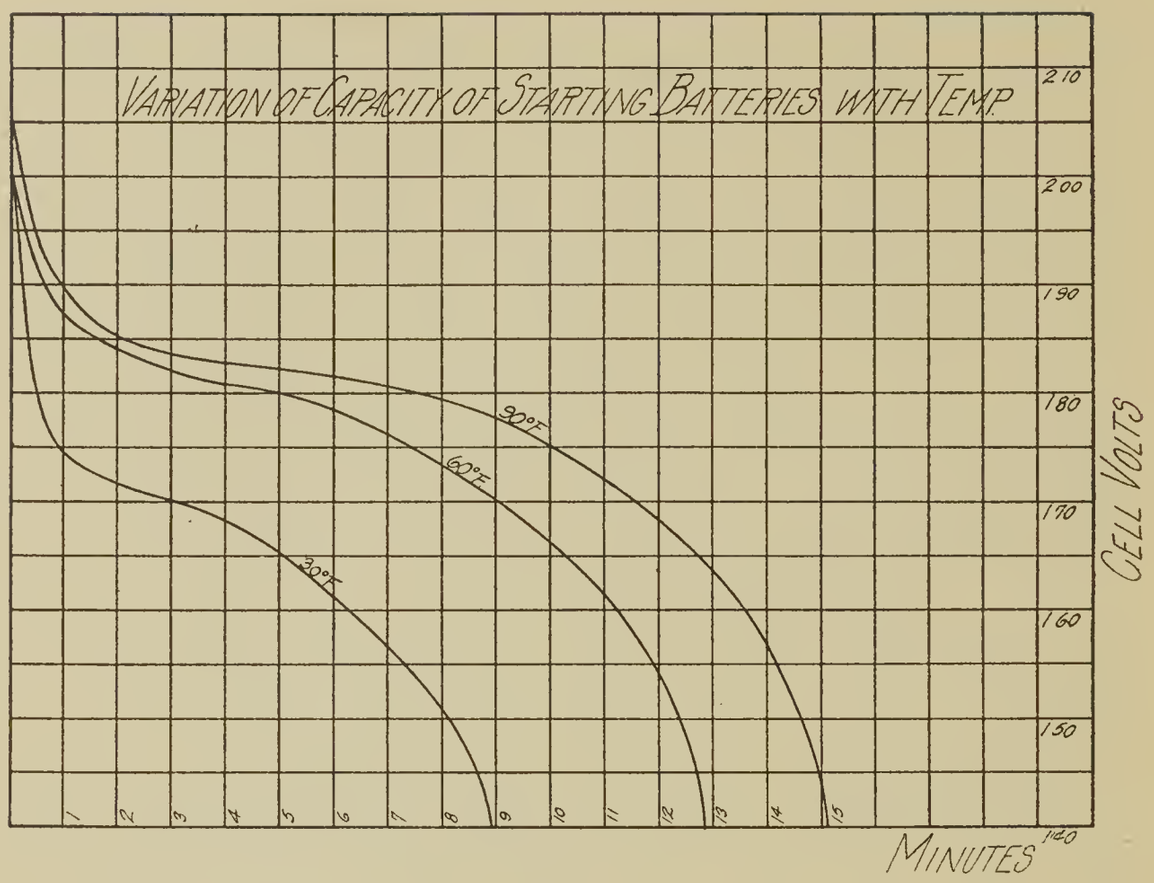


FIG. 9.

TABLE I.

Data on Competing Equivalent Starting Batteries.

Battery	No. Plates	Weight in Pounds	Space Required in Cubic Feet	Positive Area in Square Inches	Plate Volume in Cubic Inches	Capacity		Relative Voltage at 96 Amp., fully charged
						Minutes at 96 Amp. 20 Min. Rate	Hours at 5 Amp.	
A	15	52	0.415	396	18.5	28.2	19.2	5.55
B	15	51	0.452	388	18.3	27.2	20.	5.70
C	11	51.5	0.402	271	16.0	21.3	15.9	5.70
D	13	54.5	0.408	278	17.7	19.4	17.3	5.70
E	13	48	0.395	278	15.6	24.9	19.	5.75
F	13	52	0.442	278	16.7	20.9	14.6	5.75
G	13	40.5	0.393	272	17.2	26.4	18.5	5.70
H	13	50	0.415	276	19.4	25.0	18.3	5.45
I	13	55	0.440	277	20.4	23.2	18.2	5.65

Table I brings out very plainly that starting batteries of about the same size can vary considerably in construction and performance, though sold on the same rating.

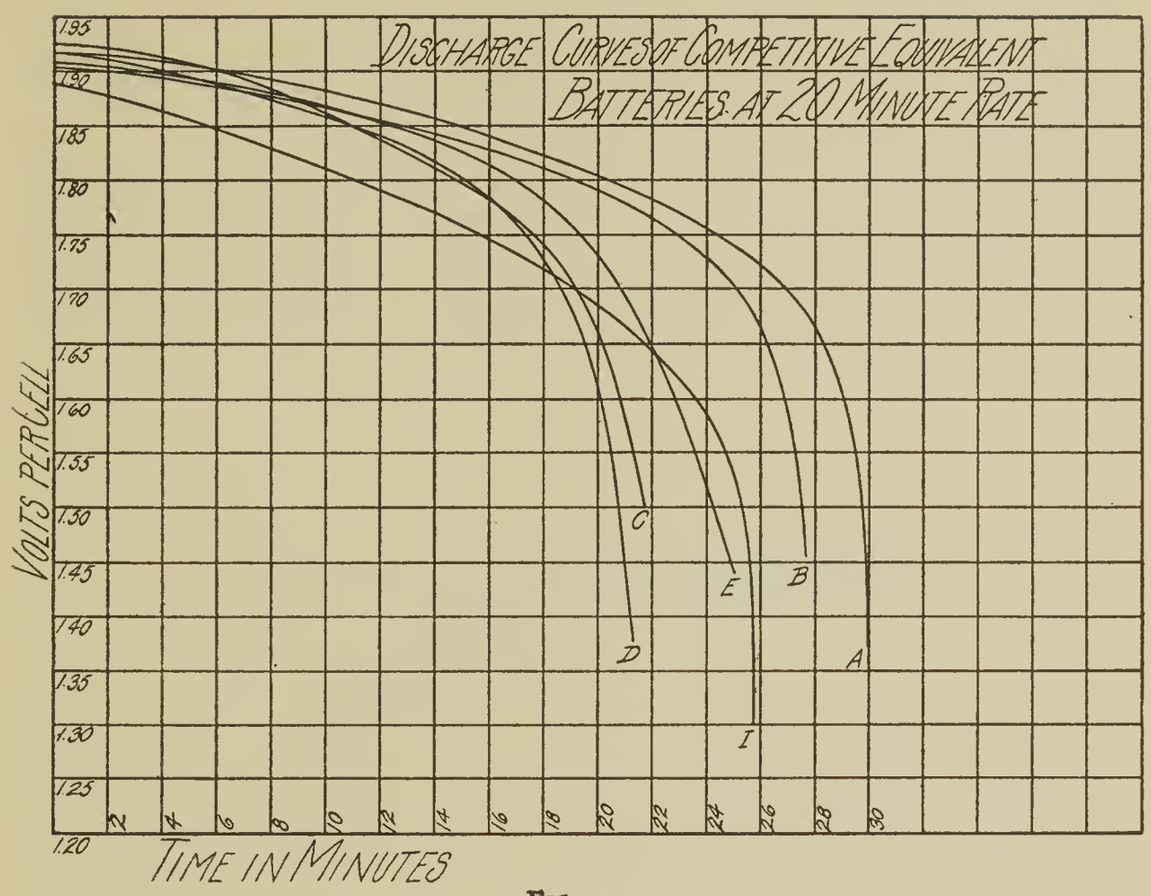


FIG. 10.

Fig. 10 shows discharge curves of competitive equivalent batteries at the 20-minute rate. These curves are samples and the data are merely comparative for one style of test, while Table I gives data which are the average of several tests on three batteries of each make.

TABLE II.

Capacity and Efficiency of Starting Batteries.

Average Temperature of Discharge, 60° F.; Charge, 80° F.
Charge and Discharge Rate, 10 Amperes.

	Capacity		Efficiency		Average Voltage		Grade on Watt Hr. Efficiency
	Amp. Hr.	Watt Hr.	Amp. Hr.	Watt Hr.	Discharge	Charge	
A	88.0	516	88.3	77.3	5.87	6.71	9.6
B	103.0	607	90.4	80.5	5.89	6.62	10.0
C	78.08	462	87.8	76.6	5.92	6.78	9.5
D	79.0	459	89.3	76.3	5.82	6.80	9.5
E	89.0	517	89.4	76.6	5.82	6.78	9.5
F	75.0	436	83.0	70.8	5.81	6.82	8.8
G	91.2	533	88.0	76.3	5.85	6.75	9.5
H	82.5	475	86.4	74.3	5.76	6.84	9.3
I	83.0	478	86.8	72.4	5.77	6.91	9.0

Fig. 11, which gives representative discharge curves of some competitive equivalent batteries at the 5-ampere rate, is like Fig. 10 in giving only representative data.

Table II gives the capacity and efficiency of competing batteries at the 10-ampere rate. While the temperatures of charge and discharge are not the same, this is a normal condition of service if the discharge does not follow the charge immediately, as it rarely does.

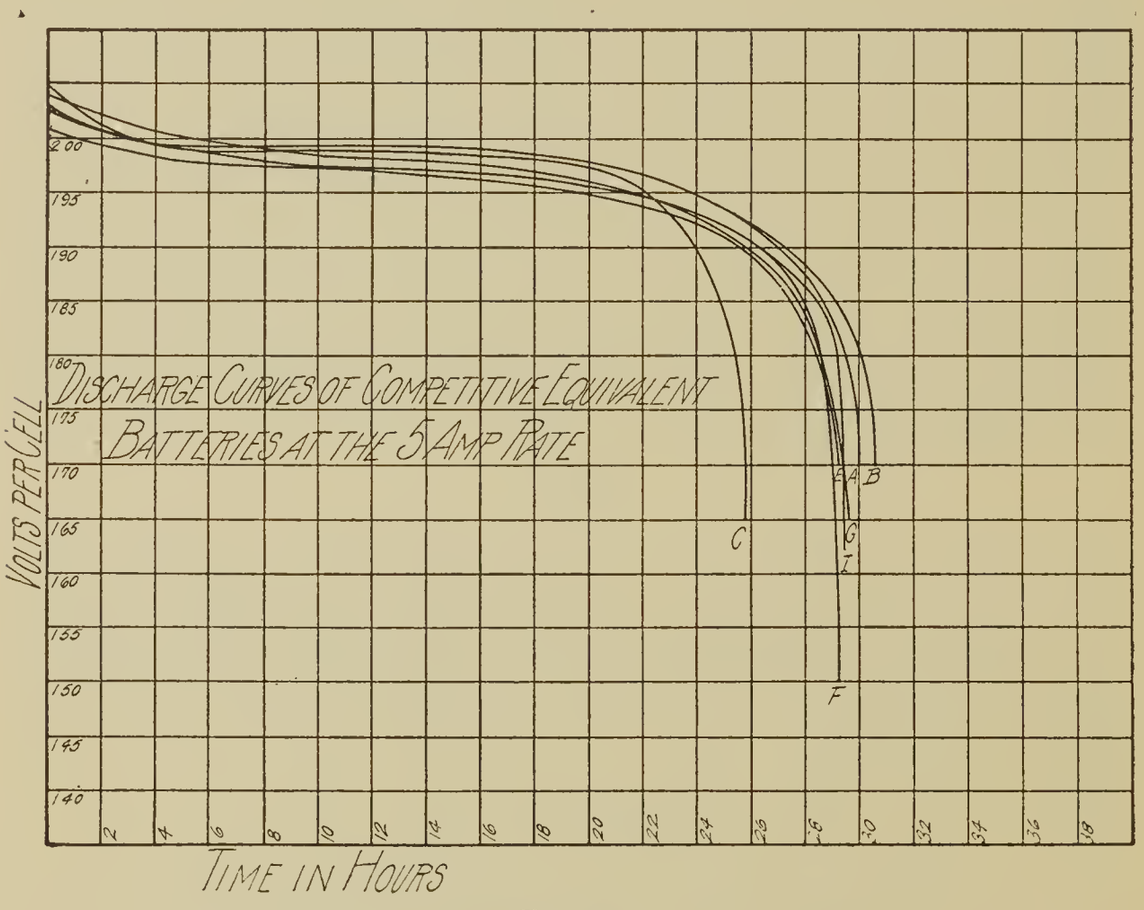


FIG. 11.

Motor Batteries.

Vehicle service requires a cell which gives the maximum capacity possible per unit of weight and space. It further requires a very tough plate in order to resist the frequent overcharging. It is by all odds the hardest service to which a battery is subjected. The money invested in each battery is sufficient to give the owner a lively interest in the life of the battery as well as in the required mileage per charge. Pleasure car owners expect at least forty miles in winter and sixty miles in summer per charge. They will recharge about twice a week, often three times, and will expect

a battery to have a life of at least 8,000 miles, which will be obtained in approximately two years without renewal of plates. Careful drivers often get 90 miles per charge in summer and 60 miles in winter, and the life of the plates under these conditions will sometimes exceed 12,000 miles. Some of this variation in capacity and life is in the plates, but most of it is due to the method of handling the car and charging outfit. Many owners who do their own recharging overcharge their batteries every time. They do this under the impression that it will give more mileage;

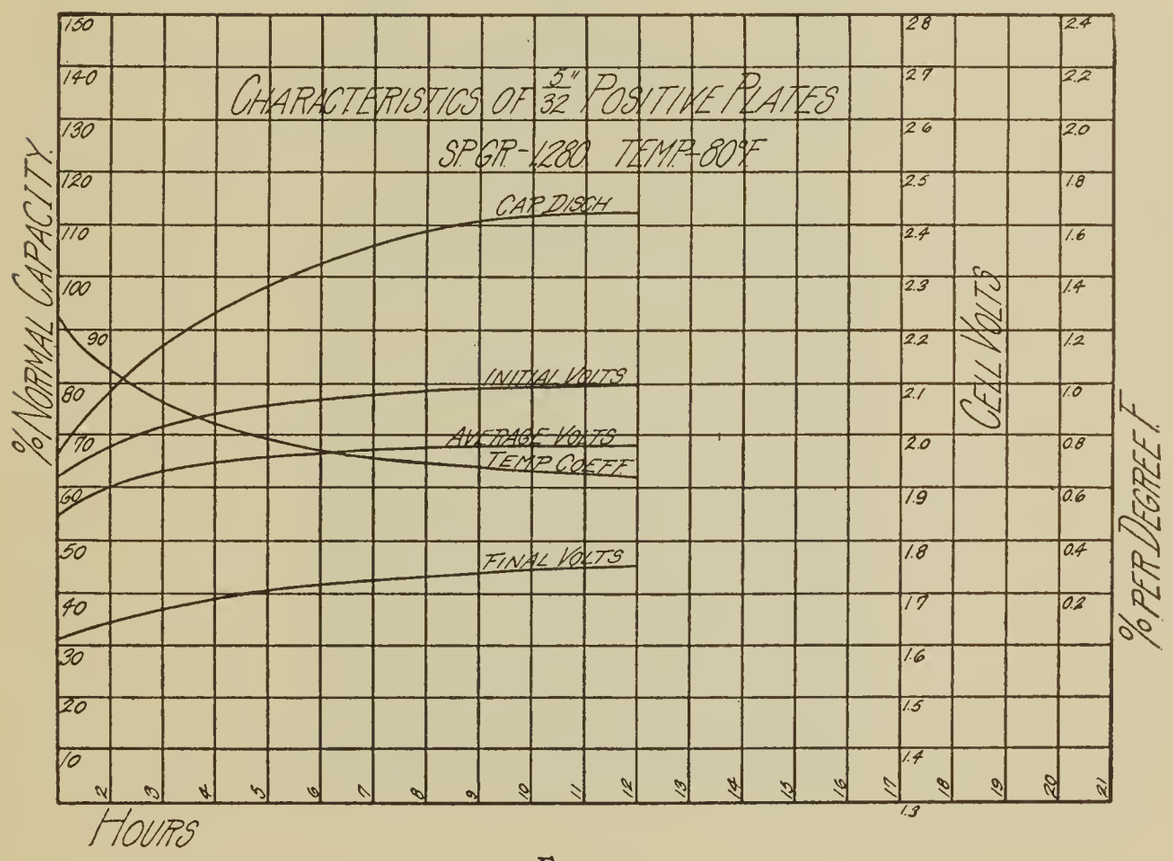


FIG. 12.

but after the charge is carried to a point where the voltage reaches 2½ volts per cell at the normal rate, or 100 volts on a 40-cell battery, further charging will not increase the mileage obtained appreciably, while it will tend to wear out the plates unnecessarily. The battery should not be overcharged oftener than every fifth or sixth charge.

Vehicle cells are composed of plates which are thicker than starting battery plates. This is necessary on account of their greater height, and because a tougher active material is required to give longer life. The harder active material requires more

grid strength to prevent buckling, also a greater reserve of positive material is needed. Vehicle positive plates vary from 9/64 to 7/32 inch (3.5 to 5.5 mm.) in thickness, while the negatives are uniformly 1/64 to 1/32 inch (0.4 to 0.8 mm.) thinner than the positive of the same type. This reduction in thickness makes a lighter cell possible.

Some curves showing the characteristics of a common vehicle plate are given in Fig. 12.

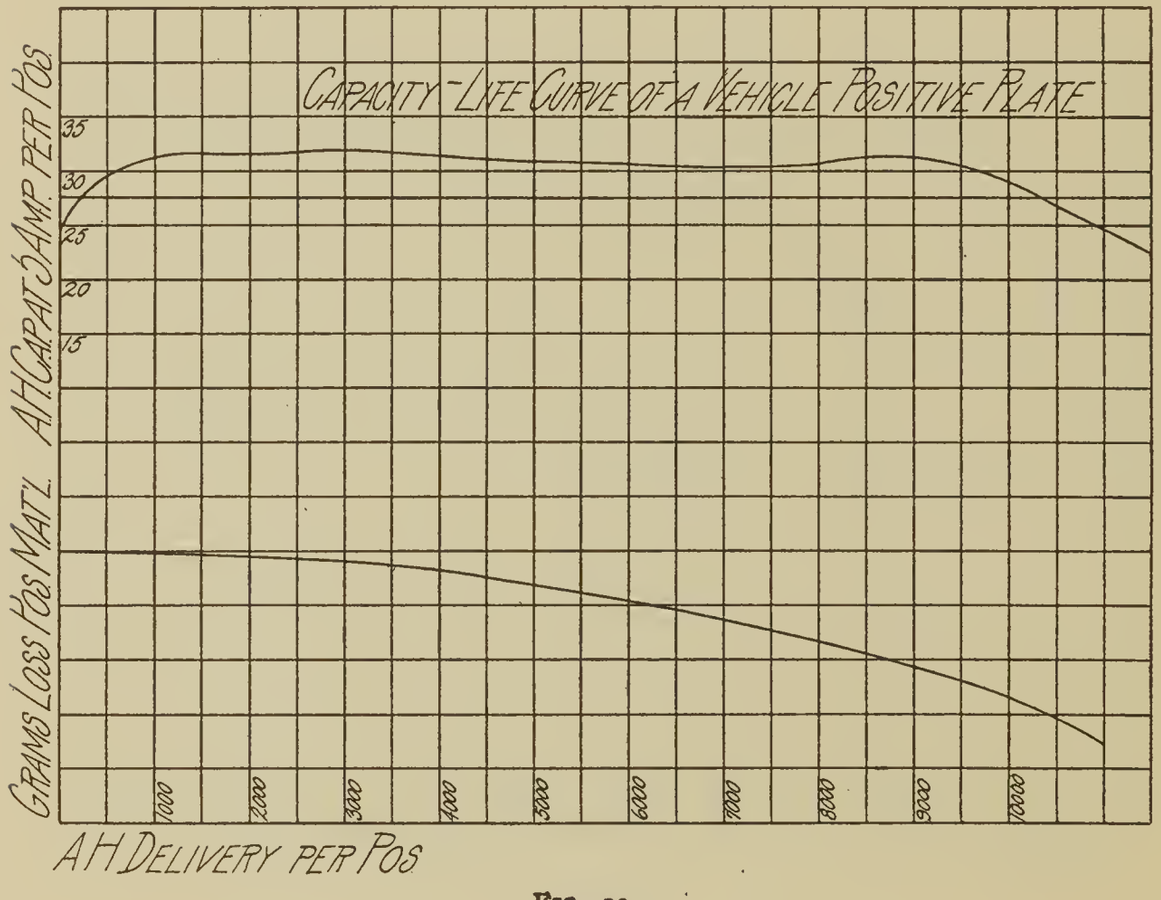


FIG. 13.

Thick vehicle plates were originally standard, positives being about 7/32 inch (5.5 mm.) thick. Then 3/16 inch (4.7 mm.) positives were developed, 5/32 inch (3.9 mm.) thickness was the next size brought out, and finally 9/64 inch (3.5 mm.) positives were introduced a few years ago. There are some 1/8 inch (3 mm.) plates now in vehicle service, though they have not been on the market long enough for a safe prediction to be made regarding their relative worth. The most popular plates at present seem to be the 3/16 and 5/32 inch (4.7 and 3.9 mm.) positives, as this size plate appears to give sufficient mileage for the aver-

age pleasure car and naturally has more reserve material than the thinner plate. However, when more of the modern electric cars of light-weight construction are in use, a smaller, thinner plate will no doubt be more economical in up-keep and replacement cost, in addition to lower energy consumption than the heavier thick plate. Plates of any thickness from 9/64 to 7/32 inch (3.5 to 5.5 mm.) should give about the same total life in ampere hours for the same weight of cell, because the thin plate, requiring less space, will present more surface and therefore for

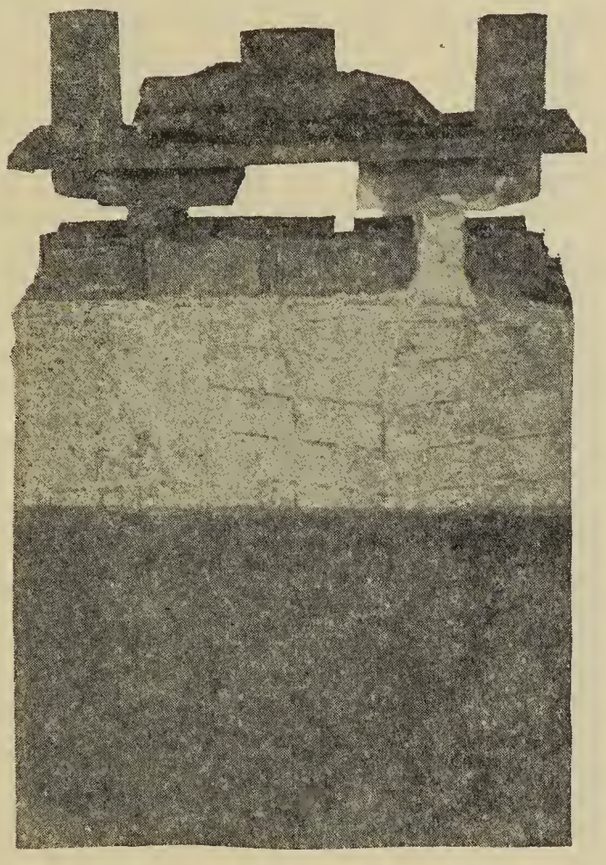


FIG. 14. Effect of Low Electrolyte.

the same service will be subject to less work per unit of area than the thick plate, and of course give more mileage per charge, though fewer cycles of life.

Fig. 13 shows the characteristic capacity life curve of a vehicle positive plate, as plotted from a laboratory test.

CAUSES OF TROUBLE AND FAILURE OF AUTOMOBILE BATTERIES.

All three classes of automobile storage batteries give excellent service, and troubles are rare where the proper sort of battery is used and well cared for. When we consider the lack of atten-

tion and heavy service required of the starting and vehicle battery, it seems remarkable that they do not give more trouble. The difficulty of insuring proper care lies in the silence of the battery, for it will accept any mistreatment and give no warning squeak or rattle to call the owner's attention, like a mechanical appliance.

Trouble is generally divided into three groups: jar, separator and plate failures. Jars only give trouble through cracks or small holes causing leaks. Small holes are eliminated by testing the

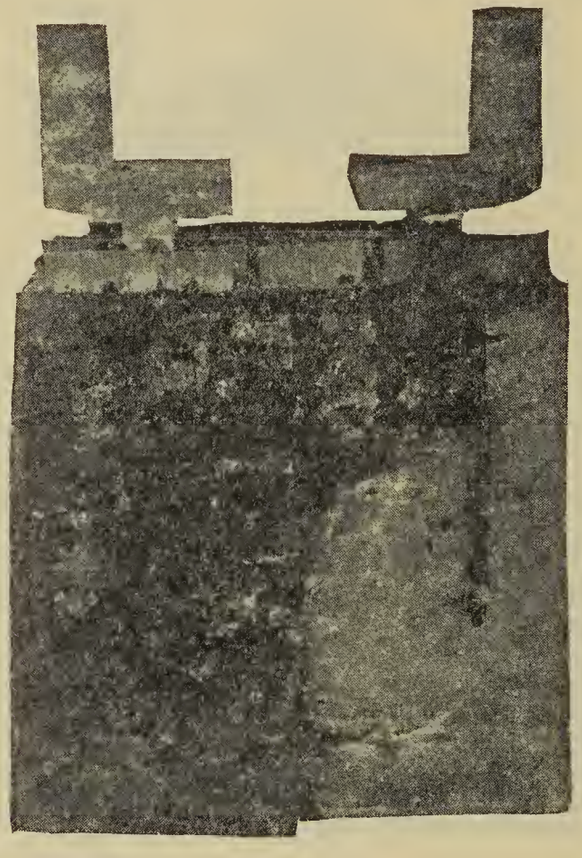


FIG. 15. Corroded Positive Grid.

jars before use. Cracks are caused by uneven pressure or blows, generally when the jars are cold. The remedy for this is of course to provide a more flexible quality of jar. The quality of material used in jars has greatly improved in the last few years.

Separators may cause failure of a cell through short-circuit or corrosion of the positive grid. Short-circuits are most frequently caused by the owner omitting to add water to his cell, with the consequence that the acid level is lowered enough to expose the upper part of the separator, which then dries and splits. When the cell is later filled with water, the active mate-

rial may short-circuit the element through the crack so formed. Corrosion of the positive grid is quite rare, though a number of cases have come to the writer's attention. There is another cause of failure due to the separator which causes most of the present battery trouble. This is softening and charring under service conditions, especially at high temperature. It occurs most frequently with soft-wood separators, and is one of the consequences of overcharging at high rates.

Positive plates fail from two chief causes: buckling and shedding or chipping. The first symptom is more prevalent in starting batteries, due to the high discharge rate and lack of sufficient charging. The plate may be literally starved for current, due to wrong setting of the generator. This condition is somewhat improved on the latest model of cars by various devices to lower the charging rates when the battery is full, which, in turn, make it possible to set the generator for a higher charging rate at low speed and when the battery is empty. Such a condition allows the growth of large crystals of lead sulphate, which being bulkier than the normal active material tend to expand the grid. This expansion may be so unequal as to cause the plate to become curved or buckled. The distance between plates being so short, this results in the corner of the plate piercing the separator, touching the adjacent plate with a short circuit. Plates may buckle though they show no sulphation as described above. In that case the trouble is probably in the active material at the start, it being too hard and not sufficiently porous for the grid supporting it. Again, the grid may not be symmetrical in design, so that normal expansion of the active material may force it out of shape along the weakest path.

Positive plates chip and shed unevenly when the active material is not uniform in structure, when heavily over-discharged, or charged at very high rates, which causes unequal expansion at rates too rapid for accommodation, or when the electrolyte is frozen. It is difficult to separate these causes in a given case, but careful examination and experience usually points out the proper clew. Shedding of the positive uniformly and evenly is a normal condition, but its rate affects the life of the plate directly. This rate may be accelerated unduly by too frequent overcharging at any current rate or by the active material being too

soft originally, or through continued over-discharging. Plates can give their full capacity when over two-thirds of their material has been shed.

Negative plates fail in three ways. They become clogged with sulphate and thus lose porosity and therefore capacity. This is caused by lack of charging, or by local discharge on open circuit, through metallic impurities. The chief offenders in this direction are copper and iron. A very small quantity of either of these

FIG. 16. Buckled Positive Plates.

metals in a cell will cause this trouble. The second cause of negative failure is shrinkage. Certain materials produce a spongy lead that is hard and of fine texture but which shrinks away from the grid early in the life of the plate, with resultant loss of capacity. The other cause of trouble is excessive expansion or blistering, which may cause the material to become so loosened that it is washed off the plate and frequently gathers as the so-called "moss" on top of the plates. A certain amount of blistering is not harmful, and it really prevents the negative material from clogging up with sulphate.

The old plague of the lead battery—"sulphation"—has been very badly overrated, and the consequence is that it is much dreaded when there is no real cause, for if a battery is overcharged two or three times a year only, there should be no permanent sulphation. Many more vehicle batteries are ruined by overcharging than through sulphation. Of course, the service stations receive some badly sulphated starting batteries, but most of these have been dry or have not received a full charge since

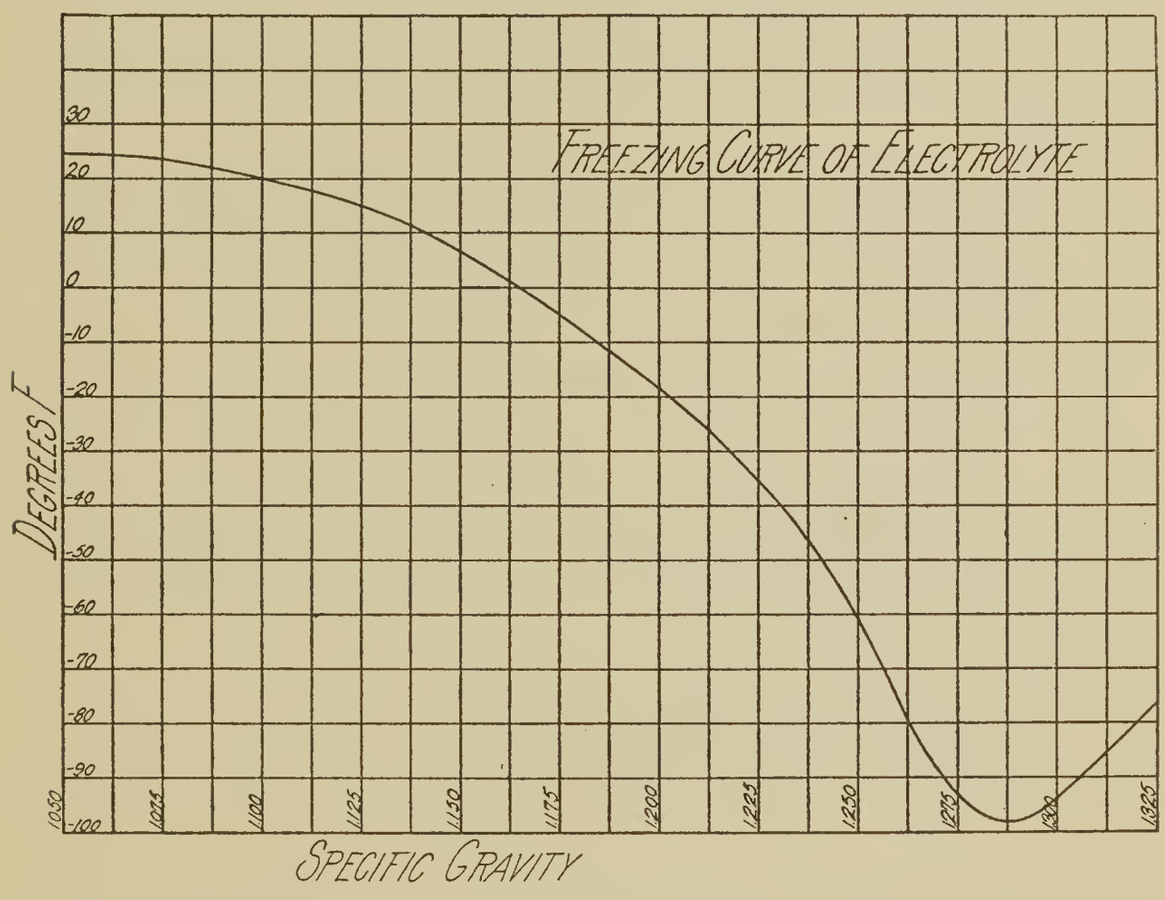


FIG. 17.

they left the factory. Even plates which are white with sulphate can usually be restored by careful charging.

The other chief cause of starting battery failures is freezing of the electrolyte. Like sulphation, there is no excuse for this occurrence as the owner should never let a battery stand discharged so low that the electrolyte is weak enough to freeze. Fig. 17 shows the freezing temperature of sulphuric acid, which illustrates this point. A battery is not normally discharged below 1.160 specific gravity.

SUMMARY AND CONCLUSIONS.

We have attempted to show the importance of automobile storage battery manufacture as an electrochemical industry, to explain some of the principles and technical problems involved, and to give some idea of the performance of each type in service. The desirable qualities in a battery for each class of service are enumerated. Some characteristic test data show the laboratory methods used and comparative results on various competing batteries of equivalent rating. The important characteristics of each type of battery are given, and their relation to design, construction and performance, with the limiting factors encountered, is outlined.

Some of the more common causes of storage battery failures are described to show the lines along which improvement can be expected, and to indicate the most favorable field for research and originality in design.

This paper is presented with the desire to introduce the automobile battery industry in a comprehensive manner to this Society. The writer hopes that it will stimulate interest in this branch of electrochemical activity, which does not seem to have received the attention it deserves as a thriving, if youthful, division of our industry.

Storage Battery Research Laboratory,
National Carbon Company.

DISCUSSION.

H. H. WILLARD[1]: One of the automobile storage battery companies lays great stress in their advertisements on the use of titanium or its compounds in their cells. I would like to inquire what the action of titanium is.

W. C. BROOKS: I have no personal knowledge of the exact action of titanium in a cell, because I have not made any tests

[1] Asst. Professor of Analytical Chemistry, University of Michigan.

on just what effect it would have, but judging from general experience and from the theory on which we work in manufacturing batteries, and from an actual observation of cells which are supposed to contain this material, I fail to see that it does any good whatever. I fail to see any reason why it would be any good.

H. H. WILLARD: Is it used in the electrolyte?

W. C. BROOKS: I understand it is supposed to be used in the active material. I may say, as I have stated in my paper, that there have been thousands of receipts published regarding materials used in storage batteries for increasing their capacity, and also the tenacity and life of the active material, but to my knowledge practically none of these are of any value. It seems as though a simple mixture of the proper sort of oxide with lead sulphate as the binding agent in the proper condition gives the best sort of plate. There are one or two things that increase the porosity and in some cases the tenacity of the material, but aside from these there are none that seem to do any good.

O. P. WATTS[2]: I would like to ask Mr. Brooks if he can express an opinion or give us any facts in regard to the claims of several battery manufacturers as to non-sulphating batteries. I have seen several advertisements, and I bought a small cell some six or seven years ago which was claimed to be non-sulphating, but it lost capacity on standing, much like the ordinary cell. The same cell is still on the market, manufactured by the same company.

W. C. BROOKS: I think that it has been in some ways an unfortunate thing for a maker to put forth such claims. The idea that was intended to be conveyed was that some particular cells have a less tendency to sulphate than others. Of course, the batteries sulphate on discharge, that is a natural occurrence, but the so-called sulphate is merely an abnormal sulphation or abnormal growth of sulphate crystals, to such a large degree that they lose their contact with the active material, and it is hard to decompose them back to the original peroxide or spongy lead on charging. If we could get an active material which through some physical property has a less tendency to grow these large crystals,

[2] Asst. Professor of Applied Electrochemistry, University of Wisconsin.

then we would have a battery without such an active tendency to sulphate permanently, and that, I think, is the direction in which some makers have been working.

H. H. SMITH[3]: My interests are with the nickel-iron battery, and I cannot let go unchallenged the remark made in the early part of the paper to the effect that this type of battery is at present restricted to certain classes of industrial truck service. Although it is a fact that the nickel-iron battery is used in fully 80 percent of the industrial electric trucks of all classes in this country, it is also true that the industrial truck consumes only a small fraction of the batteries of this type that are sold. The electric road truck, which, as Mr. Brooks truly says, is rapidly growing in popularity, the electric lighting of steam railway trains, the electric lighting of isolated homes and farms, storage battery locomotives for use in mines and industrial plants, and a number of other applications create a far larger business for the nickel-iron battery than do industrial trucks.

Perhaps some of you were more fortunate than I in being able to secure an electric taxicab to carry you from the depot to your hotel for this convention. If so it would probably interest you to know that that vehicle was propelled by means of a nickel-iron battery. Perhaps you may wonder why a taxicab company should use a battery which Mr. Brooks says is only partially successful, because of its high initial cost, knowing as you must that the taxicab business is conducted primarily for the purpose of making money and knowing also perhaps that in general the taxicab companies in this country have great difficulty in making enough to encourage them in continuing in the business. Perhaps you may wonder how this vehicle manages to keep pace with all its gas-car competitors in view of the fact that it uses a battery which Mr. Brooks states is only partially successful because of its high internal resistance. In view of the fact that you may have admired the attractive lines of this vehicle, perhaps you have been surprised to hear in this paper that the battery it uses is only partially successful because of its great bulkiness.

I think it is quite obvious that the author of this paper has been misinformed, and I am making these remarks not in the spirit of finding fault but in order that a correction may be made

[3] Edison Storage Battery Co., Orange, N. J.

before the paper is published in the Transactions of the American Electrochemical Society.

W. C. BROOKS: In answer to Mr. Smith's remarks on the Edison storage battery, the point intended to be made out was that the alkaline battery is not being produced in very large quantities compared to the lead battery, for the reason that it is considerably higher priced and takes up more space. The relatively high internal resistance of the alkaline storage battery also restricts its sale to a certain extent. For example, in automobile starting service the alkaline battery has not as yet been used, as pointed out in the paper, since all three of the restrictions mentioned above operate in this particular case.

The alkaline storage battery has been tried for several services for a number of years, and the writer still holds to the statement that compared to the lead battery, it is only partially successful, since, if it had been entirely successful, it would have dominated the field by this time. The reverse of this condition is still true, and as a concrete example we may mention electric pleasure cars, trucks and storage battery street cars, where the alkaline battery, at one time, made a strong bid for this business, but an investigation shows that a very small percentage of the total number of electric cars, trucks, and storage battery street cars use alkaline batteries.

In view of the above explanation, I do not feel that I overstated the matter when making the observation that the use of the alkaline battery is limited to certain applications, meaning that it has not come into general use because of its extra cost and space requirements, while it is further restricted in other fields on account of its relatively high internal resistance.

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, in Detroit, May 5, 1917, President FitzGerald in the Chair.

THE CURRENT EFFICIENCY IN CHARGING THE EDISON STORAGE BATTERY.

M. De Kay Thompson and L. R. Byrne.

ABSTRACT.

The objects of this investigation were to study the Edison storage battery in regard to the following points:

1. After standing a long time can it be restored to good condition by re-charging, and how long does this take?
2. Which of the two plates charges at the greater efficiency?
3. What is the effect of low temperature on this charging efficiency?
4. When is the maximum charging efficiency reached?

INTRODUCTION.

The object in the following investigation is to extend the small amount of information that is available as to the current efficiency on the separate plates in charging the Edison storage battery.

The only previous work on this subject that is known to us is a few determinations of the current efficiency on the nickel plate by Foerster (Z. f. Elektroch. (1907) **13**, 431) and on both plates by Thompson and Richardson (Trans. Am. Electroch. Soc. (1905) **7**, 100). None of these experiments was carried out on a complete cell; in both cases a part of a positive and of a negative plate were mounted in a glass vessel and the measurements were made with this arrangement.

A single cell of the B-4 type was used in the following experiments. This is a cell 20 cm. high (excluding binding posts) 13 cm. wide, and 7 cm. thick; its rated capacity is 80 amp. hours, and it has 4 positive and 5 negative plates. The normal five-hour rate of discharge is 16 amperes. This cell had been standing idle for three years before this work was begun.

The method used to determine the current efficiencies of charging each plate is the well-known one of comparing the quantities of hydrogen and oxygen evolved with the amounts of the same gases evolved in a water coulometer connected in series with the cell. In order to do this the gas must be collected from the coulometer and the cell during the same interval of time, and the volume of each measured. The gas from the coulometer is known to have the same composition as water, while the gas from the cell must be analyzed for oxygen and the hydrogen then found by difference. If no gas is evolved from the cell when a current is passed from the nickel plate through the solution to the iron plate, it must be oxidizing the nickelous oxide and reducing the iron with 100 percent efficiency; if amounts of hydrogen and oxygen equal to those evolved from the water coulometer are evolved from the cell, then evidently none of the current is used in charging. For intermediate amounts of gas the efficiency is calculated by the following formula:

$$E = 100\left(1 - \frac{b}{a}\right) = 100\left(\frac{a-b}{a}\right)$$

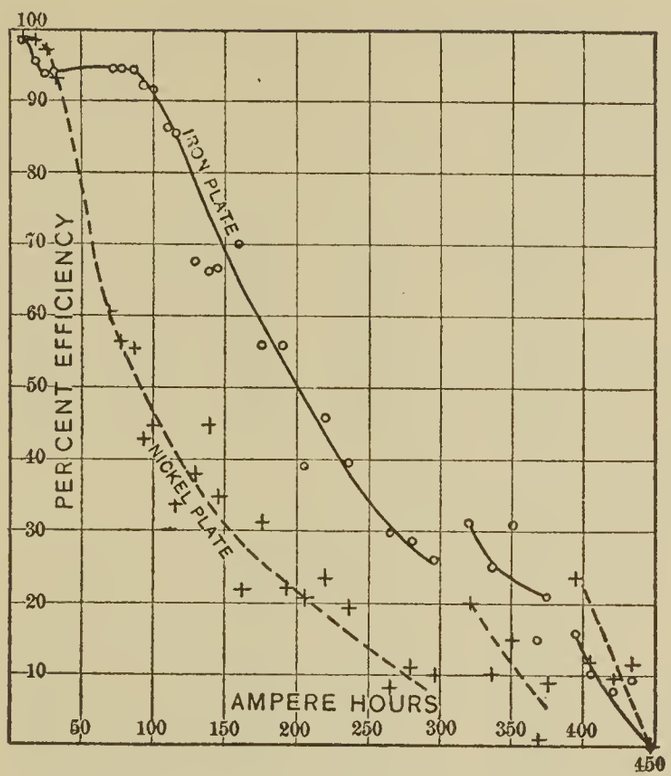
where E is the percentage efficiency on either plate, and a is the number of cubic centimeters of hydrogen or oxygen evolved by the coulometer in the same time that b cubic centimeters of the same gas are evolved by the cell.

The coulometer consisted of a glass jar containing a 15 percent sodium hydrate solution and concentric cylindrical nickel electrodes, 6 cm. high, the outer 15 cm. long (before bending into a cylinder), the inner, 10 cm.

The analysis for oxygen was made by absorption according to Hempel in a solution of pyrogallol.

TEST I.

Enough distilled water was added to the solution in the cell to fill it completely, and a charging current of 15 amperes was passed until the amounts of hydrogen and oxygen from the cell equalled those from the coulometer. The results of this run are given in Table I and Plot 1.



Charge 1. Current 15A. Temp. 18-23° C.

TABLE I. (See Plot I.)

April 5, 1916. Open Circuit—1.2 Volts; Current 15A ± 0.1.

Time	Voltage	Coulometer Gas	Battery Gas	H_2	O_2	Iron Eff.	Nickel Eff.	Temp. C°
10.15	1.56	...	..	..	..	...	...	18.5
11.00	1.68	144	2.2	1.8	0.4	98.7	99.2	18.7
11.30	1.67	144	5.0	4.3	0.7	95.5	98.5	19.3
12.00	1.72	146	7.7	6.4	1.3	93.4	97.3	19.8
12.30	1.73	146	9.0	5.6	3.4	94.2	93.0	20.3
3.00	1.72	146	24.4	5.4	19.0	94.4	60.5	22.4
3.30	1.73	150	27.2	5.6	21.6	94.4	56.8	22.6
4.00	1.73	150	28.0	5.9	22.1	94.1	55.8	22.8
4.30	1.74	150	36.3	7.8	28.5	92.2	43.0	23.0
5.00	1.74	150	35.8	8.2	27.6	91.8	44.8	23.2
5.30	1.76	114	36.7	10.2	26.5	86.6	30.3	23.2
6.00	1.76	103.5	32.6	9.9	22.7	85.7	34.2	23.2
7.00	1.77	105	44.1	22.5	21.6	67.9	38.3	23.2
7.30	1.77	100.5	41.2	22.8	18.4	66.0	45.1	23.3
8.00	1.77	108.0	47.4	24.0	23.4	66.7	35.0	23.4
9.00	1.78	107.7	49.4	21.4	28.0	70.2	22.0	23.4
10.00	1.79	104.0	54.2	30.0	23.7	56.0	31.7	23.4
11.00	1.79	78.3	43.0	22.7	20.3	56.6	22.1	23.4
	Open Circuit—1.58 Volts.							

CHARGE I. (Continued)

April 7, 1916. Open Circuit—1.52 Volts.

Time	Voltage	Coulometer Gas	Battery Gas	H_2	O_2	Iron Eff.	Nickel Eff.	Temp. C°
9.00	1.79	...	...	...	...	...	...	19.4
10.00	1.82	42.4	28.4	17.2	11.2	39.1	20.8	20.1
11.00	1.82	57.4	35.2	20.6	14.6	46.1	23.6	20.8
12.00	1.81	50.0	33.7	20.3	13.4	39.3	19.6	21.7
2.00	1.80	60.0	46.4	28.0	18.4	30.0	8.0	23.0
3.00	1.80	64.4	49.6	30.5	19.1	28.9	11.0	23.1
4.00	1.80	70.3	55.4	34.3	21.1	26.7	10.0	23.2
4.30	1.80	...	...	...	...	...	...	23.3
	Open Circuit—1.58 Volts.							

April 12, 1916. Open Circuit—1.44 Volts.

11.45	1.70	...	...	...	...	...	...	19.0
1.00	1.83	78.0	56.6	35.8	20.8	31.1	20.0	20.3
2.00	1.82	55.0	44.0	27.6	16.4	24.9	10.2	21.4
3.00	1.81	57.8	42.8	26.5	16.3	31.2	15.5	22.6
4.00	1.81	48.6	43.0	27.0	16.0	15.4	1.2	23.6
4.30	1.81	45.2	37.4	23.7	13.7	21.5	9.1	24.0
	Open Circuit—1.56 Volts.							

April 13, 1916. Open Circuit—1.52 Volts.

9.00	1.67	...	...	...	...	...	...	18.7
10.00	1.83	46.4	37.8	26.0	11.8	16.0	23.9	19.5
11.00	1.83	46.5	41.6	27.8	13.8	10.3	11.0	20.6
11.00	Open Circuit—1.60 Volts.							
2.00	Open Circuit—1.51 Volts.							
2.00	1.73	...	...	...	...	...	...	20.4
3.00	1.82	58.4	53.5	35.9	17.6	7.7	9.7	21.0
4.00	1.82	50.4	48.7	33.4	15.3	9.0	11.9	21.8
4.45	1.81	43.5	43.2	30.5	12.7	.0	.0	22.2
	Open Circuit—1.61 Volts.							

Discharge I.

April 14, 1916. Open Circuit—1.46 Volts.

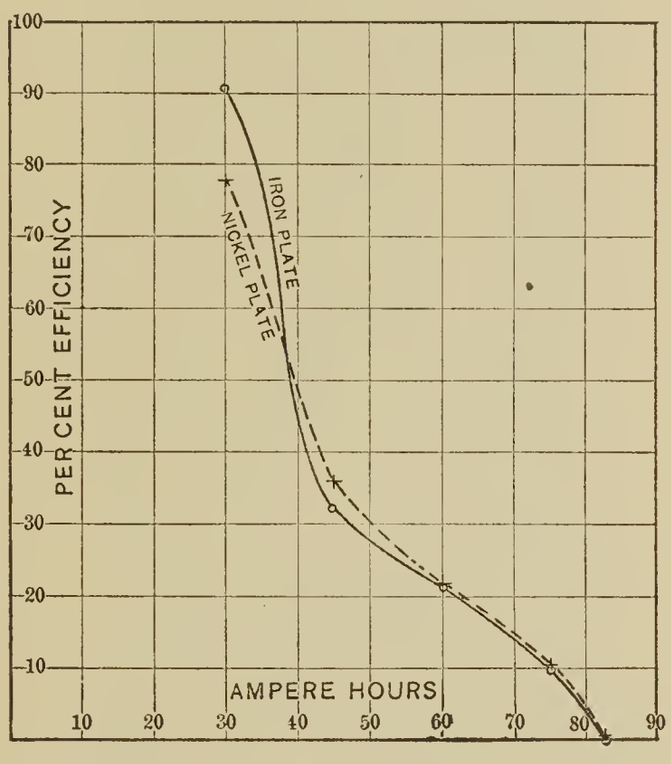
40 ampere-hour discharge at 10.0 amperes, and at 20.4° C.

Open Circuit—1.33 Volts.

In all, 446 ampere hours was passed through the cell before it was completely charged. This charging had to be interrupted several times on account of its length. The table shows that when charging was again started it was necessary to put in from 15 to 30 ampere hours before reaching the composition of gas evolved at the time the previous charging was stopped.

The battery was allowed to discharge, on April 14th, 40 ampere hours at 10 amperes. The open-circuit voltage fell from 1.46 to 1.33.

The battery was then charged again. The results are given in Table II and Plot II. 82.5 ampere hours was required to charge fully. The current efficiency of the whole battery was, therefore, 48.5 percent.



Charge 2. Current 15A. Temp. 18-23° C.

TABLE II. (See plot II.)

April 14, 1916. Open Circuit—1.32 Volts; Current 15A ± 0.1.

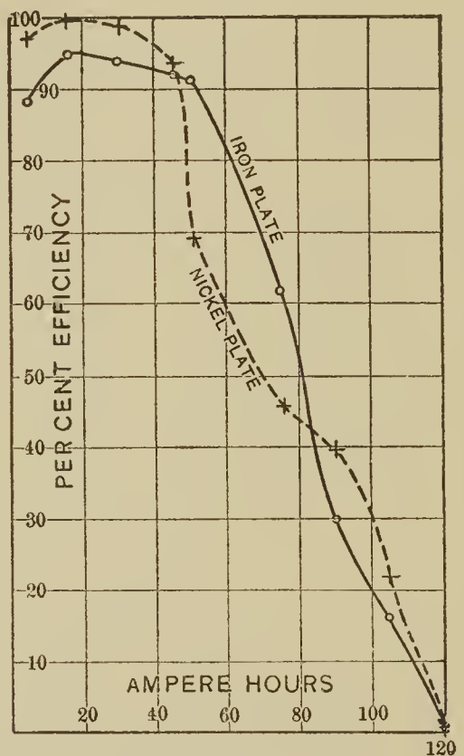
Time	Voltage	Coulometer Gas	Battery Gas	H_2	O_2	Iron Eff.	Nickel Eff.	Temp. C°
4.00	1.58	...	...	...	...	...	...	19.5
6.00	1.71	134.6	18.3	8.4	9.9	90.7	77.9	21.0
7.00	1.81	64.3	42.7	29.0	13.7	32.3	36.0	21.6
8.00	1.81	65.8	51.8	34.7	17.1	21.0	21.55	22.2
9.00	1.81	60.7	54.6	36.6	18.0	9.7	10.9	22.7
9.30	1.81	52.8	52.8	35.7	17.1	0	0	22.8
		Open Circuit as follows:						
9.30	1.68							
9.35	1.56							
9.40	1.55							
9.50	1.54							

Discharge II.

April 17, 1916. 80 Ampere-Hour Discharge at 3.6A, at 20° C.
Open Circuit—1.26 Volts.

April 17th, the battery was allowed to discharge 80 ampere hours at 3.6 amperes, after which the open-circuit voltage was 1.26.

It was then charged again. The results are given in Table III and Plot III. 120 ampere hours brought the battery back to the fully charged state, giving a current efficiency of 66.7 percent.



Charge 3. Current 15A. Temp. 18-23° C.

TABLE III. (See Plot III.)

April 18, 1916. Open Circuit—1.26 Volts; Current 15A ± 0.1.

Time	Voltage	Coulometer Gas	Battery Gas	H_2	O_2	Iron Eff.	Nickel Eff.	Temp. C°
3.00	1.65	...	...	...	...	...	...	19.8
3.15	1.67	269.0	24.2	21.6	2.6	88.0	97.1	19.9
4.00	1.68	280.0	9.8	9.4	0.4	95.0	99.6	20.3
5.00	1.68	275.0	11.0	10.0	1.0	94.5	98.9	20.9
6.00	1.70	141.0	10.7	7.6	3.1	91.9	93.4	21.1
7.00	1.73	141.0	23.0	8.4	14.6	91.1	69.0	21.3
8.00	1.79	110.0	47.8	28.0	19.8	61.8	45.9	21.6
9.00	1.81	42.3	28.3	19.8	8.5	29.8	39.7	22.0
10.00	1.81	37.5	30.8	21.0	9.8	16.0	21.6	22.1
11.00	1.81	31.7	31.5	21.2	10.3	0	0	22.3

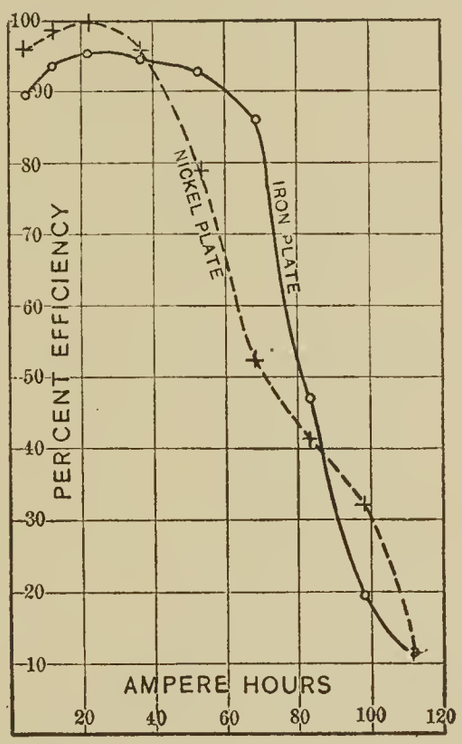
Discharge III.

April 20, 1916. 80 Ampere-Hours at 3.65A, at 20° C.

Open Circuit—1.26 Volts.

April 20th, the battery was allowed to discharge 80 ampere hours at 3.65 amperes, after which the open-circuit voltage was 1.26.

The results of the next charging are given in Table IV and Plot IV. This run shows the same general course as run 3.



Charge 4. Current 15A. Temp. 18-23° C.

TABLE IV. (See Plot IV.)

April 21, 1916. Current 15A ± 0.1.

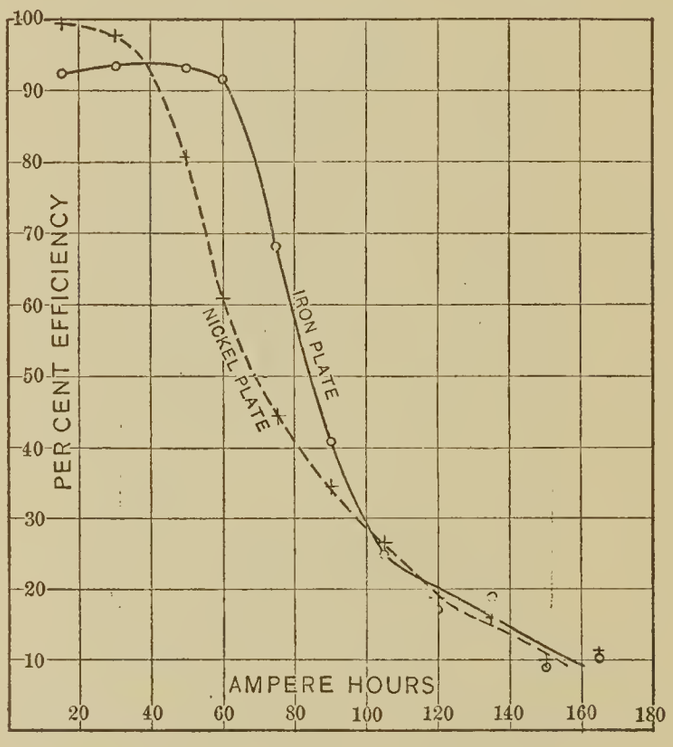
Time	Voltage	Coulometer Gas	Battery Gas	H_2	O_2	Iron Eff.	Nickel Eff.	Temp. C°
9.30	1.69	...	...	...	...	...	...	19.3
9.45	1.68	144.0	12.0	10.1	1.9	89.5	96.0	19.4
10.15	1.68	279.0	12.4	11.3	1.1	93.9	98.8	19.5
11.00	1.68	274.0	8.5	8.0	0.5	95.6	99.4	20.1
12.00	1.69	281.0	14.6	11.0	3.6	94.1	96.2	20.8
1.00	1.70	141.0	16.6	6.6	10.0	93.0	78.7	21.7
2.00	1.75	106.0	27.0	10.1	16.9	85.8	52.2	22.5
3.00	1.79	46.4	25.5	16.4	9.1	47.0	41.3	23.0
4.00	1.80	35.6	27.4	19.1	8.3	19.4	30.2	23.6
5.00	1.81	37.6	33.2	22.1	11.1	11.2	11.9	24.2

Discharge IV.

April 25, 1916. 80 Ampere-Hours at 4.5 A, at 20° C.

The battery allowed to discharge 80 ampere hours at 4.5 amperes was then charged at a temperature of from 2 to 5° C., with

the results given in Table V and Plot V. It required 165 ampere hours to bring it back to the fully-charged state, giving a current efficiency of 48.5, or a lowering of 20 percent from that at 20° C. This can be due to nothing other than a reduction in the velocity of the chemical reaction. A reduction in the reaction velocity must be the reason this battery does not work well in cold weather, not a reduction in the open-circuit voltage.



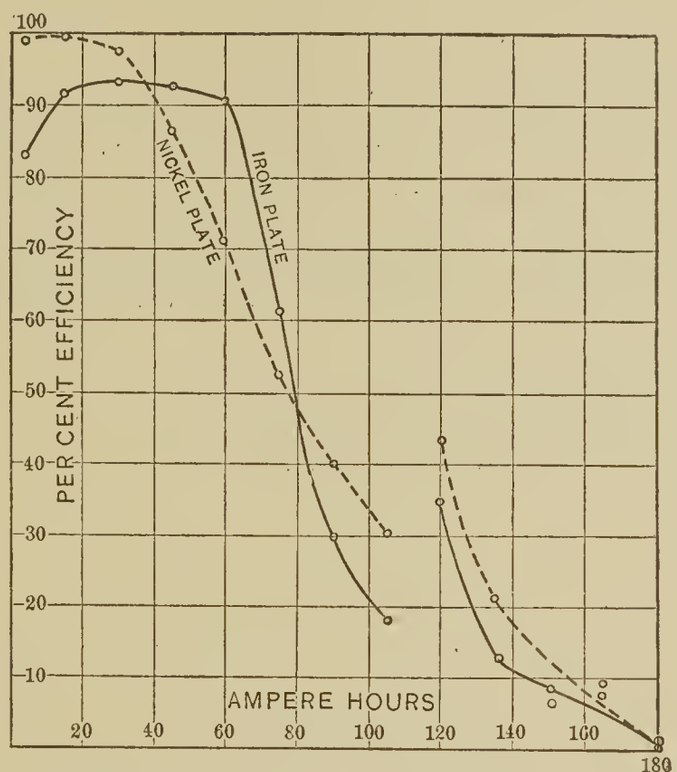
Charge 5. Current 15A. Temp. 3-5° C.

TABLE V. (See Plot V.)

May 10, 1916. Open Circuit—1.18 Volts; Current 15A ± 0.1.

Time	Voltage	Coulometer Gas	Battery Gas	H_2	O_2	Iron Eff.	Nickel Eff.	Temp. C°
11.00	1.37	...	...	...	...	...	...	3.2
12.00	1.75	287.0	14.8	14.3	0.5	92.5	99.5	2.2
1.00	1.78	285.0	14.6	12.6	2.0	93.4	97.9	5.0
2.00	1.78	145.0	15.6	6.7	8.9	93.1	80.7	3.0
3.00	1.81	110.0	20.5	6.1	14.4	91.7	60.8	4.1
4.00	1.84	56.0	22.2	111.8	10.4	68.3	44.4	5.1
5.00	1.86	48.3	29.5	19.0	10.5	41.0	34.8	2.3
6.00	1.87	32.0	23.7	15.8	7.9	25.8	26.2	2.0
7.00	1.87	33.6	27.7	18.5	9.2	17.4	17.8	5.0
8.00	1.87	40.2	32.8	21.5	11.3	19.8	15.7	5.0
9.00	1.87	26.8	24.3	16.2	8.1	9.5	9.3	5.1
10.00	1.87	27.0	24.3	16.2	8.1	10.0	10.0	4.5
	Open Circuit—1.45 Volts.							

375 ampere hours was then taken from the battery and a duplicate run at the same temperature as run 5 was made. The results are in Table VI and Plot VI. The agreement is not particularly good.



Charge 6. Current 15A. Temp. 2-5° C.

TABLE VI. (See Plot VI).

May 19, 1916. Open Circuit—1.26 Volts; Current 15A ± 0.1.

Time	Voltage	Coulometer Gas	Battery Gas	H_2	O_2	Iron Eff.	Nickel Eff.	Temp. C°
10.30	1.65	...	...	...	...	...	...	2.5
10.45	1.74	143.0	16.3	16.0	0.3	83.2	99.4	2.5
11.30	1.76	284.0	14.6	14.3	0.3	92.4	99.7	2.5
12.30	1.76	288.0	14.0	12.0	2.0	93.7	97.9	3.0
1.30	1.77	147.0	13.5	7.0	6.5	92.7	86.7	4.0
2.30	1.79	147.0	22.8	8.8	14.0	91.0	71.4	3.0
3.30	1.84	46.9	19.4	12.0	7.4	61.7	52.6	3.5
4.30	1.86	33.9	22.5	15.8	6.7	30.1	40.7	5.0
5.30	1.87	32.0	24.8	17.4	7.4	18.3	30.8	4.0
		May 22, 1916. Open Circuit—1.44 Volts.						
11.00	1.65	...	...	...	...	...	...	4.0
2.00	1.88	53.4	33.0	23.0	10.0	35.4	43.7	4.0
1.00	1.89	44.0	37.0	25.5	11.5	13.0	21.8	3.5
2.00	1.90	30.9	28.5	19.1	9.4	7.3	8.7	4.0
3.00	1.90	33.0	30.3	20.3	10.0	7.7	9.1	4.0
4.00	1.90	42.0	42.0	28.0	14.0	0	0	4.0
	Open Circuit—1.60 Volts.							

SUMMARY.

The results of this work show:

1. That an Edison battery after standing for a long while requires a long charge to get it into good condition, and that the battery can be restored by this treatment.

2. At room temperature the efficiency of charging the iron plate is in general greater than that for the nickel plate.

3. At low temperature the efficiency of charging is reduced.

4. On starting the charging a maximum in the efficiency for both plates is reached in the early part of the charge.

Electrochemical Laboratory,
Massachusetts Institute of Technology,
Cambridge, September, 1916.

DISCUSSION.

W. C. BROOKS[1]: I have had to handle a number of Edison batteries in a service station for electric pleasure cars. I found in actual practice that we had to periodically overcharge an Edison battery as well as a lead battery, to keep up its capacity, otherwise it seems to get sluggish, its internal resistance apparently being increased. The chief difference is that you have to overcharge the Edison battery at a high rate. Low-rate charging does not seem to produce the desired effect. For instance, in an Edison battery which has a 30-ampere rate for seven hours, the overcharge, instead of being reduced to a low amperage, as it should be in the case of the lead battery, must continue at the full rate. I have heard in explanation that this tendency to lose capacity, which is similar to sulphation in the lead battery, is caused by a crust of either potassium carbonate or potassium hydroxide formed in or on the positive plate.

H. H. SMITH[2]: This paper is a very interesting addition to the literature of the Edison storage battery. A great deal of interest

[1] Storage Battery Engineer, National Carbon Co., Cleveland.
[2] Edison Storage Battery Co., Orange, N. J.

attaches to the consideration of some of the scientific phenomena involved in the operation of this battery. It is altogether to be desired that more work along these lines be conducted by independent and disinterested scientists. We usually find that the manufacturer of an article of this kind is more interested in considerations that have to do with commercial development or commercial operation. He is rather busily occupied with these problems both for his own information and for the information of his customers. For their purposes the efficiency of a complete cell under normal operating conditions is more to the point than the efficiency of the individual positive or negative electrode. Furthermore, a charge carried to what we might call "absolute" completion is not practical. It is obvious from the curves herein presented that a shorter charge is more efficient, and that beyond a certain point charging is wasteful. It is for this reason that seven hours or less is the normal length of the charging period.

Looking at this subject from the practical standpoint, it seems to me that the most significant conclusion which has been drawn is that this battery, after standing for three years in an idle condition, could be restored to useful activity. This is one respect in which the alkaline battery makes a radical departure from the ways of the older types. Another point of interest which is not developed very clearly, but which is borne out by other investigations, is that a cell under these conditions improves during several successive runs. This is shown, in the results reported, by the increase in efficiency. Furthermore, it may be noted that in Plot I the relative shapes of the nickel and iron curves differ quite materially from those shown in subsequent plots. This shows that as the temporary sluggishness which resulted from the long period of idleness is gradually overcome, the positive and negative electrodes become more and more evenly balanced. This necessarily leads to the thought that owing to the changes that are taking place the results are not truly representative of the behavior of the Edison battery in its normal condition.

The statement made on page 346 is, I fear, just a little unhappily expressed. It is really not a fact that this battery does not work well in cold weather. There is unquestionably a reduction in the reaction velocity if the battery becomes cold, and this result is shared in perhaps all electrochemical processes of a simi-

lar character. The fact, however, that Edison batteries are used for the propulsion of electric vehicles in such localities as Winnipeg, where temperatures remain at 35 and 40 degrees below zero Fahr. (— 37 to — 40° C.) for three and four weeks at a time makes it plainly evident that the effect of cold is not serious from the standpoint of commercial operation.

Inasmuch as the paper under discussion sets forth results that were obtained from a very few experiments, conducted with a cell whose characteristics were apparently undergoing more or less rapid change, it is to be hoped that investigators may consider it desirable to go further into the subject.

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 5, 1917, President FitzGerald in the Chair.

A CUPROUS OXIDE PHOTO-CHEMICAL CELL.

By Theodore W. Case.

[*Abstract.*]

A large number of electrolytes were found which deposit by immersion upon copper a light-active coating, probably due to the formation of a copper oxide or halide salt upon the electrode. A copper formate electrolyte, containing free formic acid, using highly polished copper electrodes was studied closely. If one plate be illuminated and the other kept dark a current is produced, the illuminated plate being anode, and developing an E. M. F. up to 0.11 volt. The current finally drops to zero; but if the cell is rotated, illumining the previously dark plate, the E. M. F. reappears. On continued rotation the E. M. F. reaches a maximum value. Below a critical light intensity the cell gives very little response. The theory of the reaction is discussed.

INTRODUCTION.

A large amount of work has been done on cells that produce an E. M. F. on exposure to light. Becquerel,[1] the pioneer in this field, and later Minchin,[2] and others[3] found that a large number of combinations could be developed that would produce a current under the influence of light. They worked out in detail a number of light-active cells consisting of silver salts upon some metal plate, and in these they observed certain peculiar reversals of current which they were unable to explain. These difficulties were later studied by Wildermann,[4] who worked out equations applying to the action of photo-chemical cells, starting with the fundamental conception, "that the chemical potential of a substance in light and dark is different, becoming greater in light."

[1] See References, at end of paper.

In nearly all of these photo-chemical cells the output was very small (amperes in units of 10^{-9}, and volts in units of 10^{-6}). This, together with the unsatisfactory action, the ultimate consumption of the elements, and the difficulty of accurate observation of the actual processes taking place due to complicated side reactions, has tended to check research in this field. Since, however, the more photo-chemical reactions that are known, with their different modes of action, the more chance we have to understand the phenomena, the author has undertaken a search for new substances and combinations which show a voltage effect in light.

EXPERIMENTAL.

Part I.

A systematic search was begun in the first instance with copper salts. Small pieces of carefully cleaned copper wire were immersed in a large number of solutions, covering nearly all the common acids, bases, and salts, of concentration varying from very dilute to saturated, for a period of twelve hours. These wires were then taken out of the solutions and mounted separately upon small corks close to a polished silver wire. This combination, consisting of the coated copper wire and the clean silver wire, when tap water is allowed to drip upon the wires, produces a miniature cell. Any electrolyte may be substituted for the tap water by placing a strip of blotting paper behind the wires and pouring the electrolyte upon it. These cells were tried for photo-activity upon an audion apparatus, the arrangement of which is unique to this laboratory, and will be briefly described.

An arc lamp and a variable-speed water-motor are mounted upon a concrete base. The water-motor drives a disk which has 15 sectorial equidistant openings, which serve to interrupt rapidly the concentrated beam of light produced by the arc and brought to focus upon the cell under observation. Lead wires run from this cell to an Ayrton shunt which is connected to a Type P-3, three-step, De Forrest audion amplifier. High-resistance receivers can be inserted in any one of the three steps; and, if any photo-chemical action be produced by the interrupted beam of light upon the cell, a distinct note is heard in the receivers. With this apparatus it is possible to try a large number of combinations in a short period of time; and, from the intensity and

variations of the note heard, a qualitative action of the cell can be obtained.

A large number of electrolytes were found which would deposit a light-active coating upon copper, and with possibly two exceptions this could be attributed to the formation of an oxide or a halide salt upon the wire. The outstanding feature to be observed is that the electrolyte used may be the same as that which coats the copper wire with the reactive salt. This has an important bearing upon the fatigue and consumption of the elements of a light-active cell. The combinations found to give an E. M. F. in light on the audion apparatus were then tried in cells of a larger size, consisting of polished copper plates in solutions of the electrolyte. One combination that showed a large light action was made up of polished copper plates in a slightly acid copper formate solution. This cell will now be discussed in detail in the remainder of the paper.

EXPERIMENTAL.

Part II.

When a solution of copper acetate is electrolyzed between copper electrodes, a precipitate of hydrous cuprous oxide and cupric oxide is formed, the composition depending upon the conditions of temperature, current density, and concentration of the electrolyte.[5] This also occurs when a solution of copper formate is used as the electrolyte, in which case cuprous oxide is more readily formed, and comes down as a red coating on the anode. In the wire tests of Part I the author found that this oxide appeared instantly upon the copper by mere immersion, although the coatings would not become as thick as when the copper salt is electrolyzed.

With this reaction as a basis, the copper formate cell was made. This in its final form consisted of two copper plates of very pure copper. These plates were carefully cleaned of foreign matter and any copper salts by immersion first in a strong alkaline solution and then in nitric acid, followed by polishing with steel wool. Best results were obtained when the surface of the plate was highly polished and very smooth. After cleaning, the electrodes were bound into a unit with cotton thread and separated with sheet mica as an insulator.

The electrolyte was made of C. P. crystallized copper formate dissolved in cold distilled water to give a 2.5 percent solution, and a small amount of formic acid added (usually not more than 0.5 percent of 80 percent $H.CO_2H$). The plates as prepared above were immersed in this electrolyte, held in some suitable container at a temperature of about 38° C. In this work, the electrodes were copper sheets 1¾ inches (4.4 cm.) wide, 9 inches (23 cm.) long, and 0.008 inch (0.2 mm.) thick. These were immersed in a glass cell containing 250 c.c. of electrolyte. As soon as these plates are immersed, a thin orange-colored coating

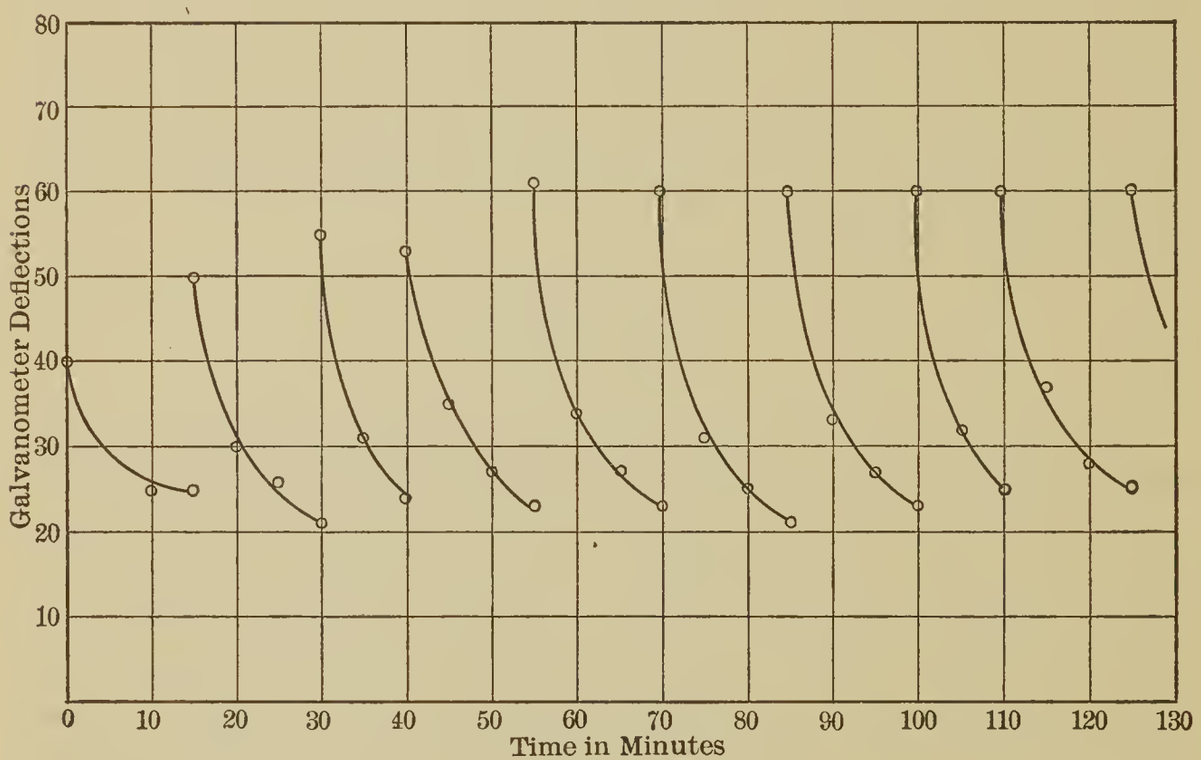


FIG. 1.

forms on the surface. If the cell be connected to a current measuring instrument, and one plate illuminated (preferably in sunlight or in light of equal intensity) while the other be kept dark, a current will be produced, the exposed plate acting as anode. The voltage of the cell is 0.11 volt or slightly over, and the current will depend upon the size of the electrode. Plates 8 inches by 1¼ inches (20 x 3.2 cm.) give about 0.003 ampere.

As stated above, the front or exposed plate acts as the zinc electrode of a copper-zinc galvanic cell, in other words is the negative or oxidizable electrode. This action of cuprous oxide should be contrasted with the short-lived action of a cupric oxide

plate under the influence of light in the same electrolyte, which is the exact opposite and which becomes the positive or deoxidizable electrode. The cuprous oxide electrode, then, under illumination, is the oxidizable electrode, and the current flows in the solution from the illuminated to the dark plate.

Under continuous exposure this first illuminated plate fatigues, and finally the current drops nearly to zero. The active material of the electrode has been consumed and rendered inactive as in other photo-chemical cells upon continuous exposure. But, if the cell be reversed so that the previously unexposed plate is illuminated, an E. M. F. is produced with this plate acting as anode. This E. M. F. will fall slowly upon continued illumination and then the cell should be rotated back to its original position, with the formerly exhausted plate exposed again. This cell will be found not only to have recovered entirely, but even to be more active than at first. Upon continued rotation as the plate fatigues the current finally reaches a maximum value. The following is a characteristic run giving interval of rotations, galvanometer and voltage readings:

Time in Minutes.	Plate 1. Galvanometer.	Volts.		Plate 2. Galvanometer.	Volts.
0	40	0.06		..	...
10	25	0.04		..	...
15	25	0.04	On turning	50	0.08
20	..	...		30	0.04
25	..	...		26	0.04
30	55	0.08	On turning	21	0.03
35	31	0.04		..	...
40	24	0.035	On turning	53	0.09
45	..	...		35	0.045
50	..	...		27	0.04
55	61	0.085	On turning	23	0.035
60	34	0.045		..	...
65	27	0.045		..	...
70	23	0.035	On turning	60	0.085
75	..	...		31	0.045
80	..	...		25	0.04
85	60	0.085	On turning	21	0.03
90	33	0.045		..	...
95	27	0.045		..	...
100	23	0.03	On turning	60	0.09
105	..	...		32	0.04
110	60	0.085	On turning	25	0.04
120	28	0.04		..	...
125	25	0.04	On turning	60	0.09

This action is shown graphically by the curve in Fig. 1. Such a cell has been kept running in light for a period of six weeks, without diminishing of the current and voltage readings. If the cell be left standing for a long time without use, the coatings on the plates gradually thicken, become darkened and inactive.

There seems to be a critical light intensity below which the cell shows very little action. This action is directly opposite to that of a photo-chemical cell having copper electrodes with a cupric oxide coating, which is extremely active in a low intensity of light. These cells also show a difference as to the part of the spectrum in which they are most sensitive. The cuprous oxide cell is most sensitive in the region of the shorter wave lengths of

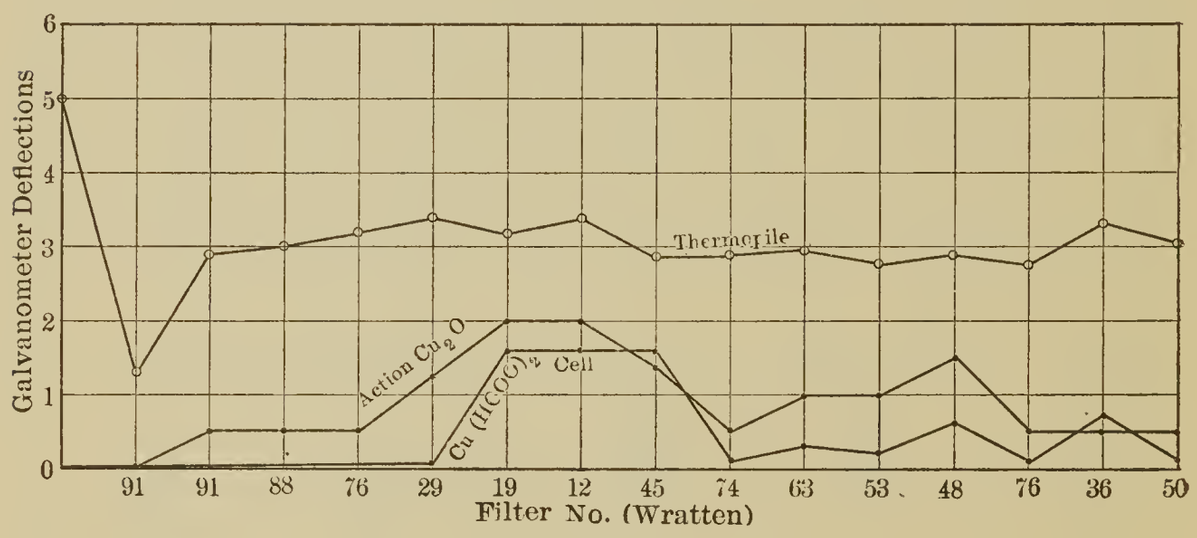


FIG. 2.

light, while the cupric oxide is most sensitive to the red end. The action of the cuprous oxide photo-chemical cell agrees with that found by Pfund[6] for the change of resistance of cuprous oxide. The curves on Fig. 2, for the action of the cell and of cuprite (mineral Cu_2O), tend to show this point. These curves were made from data obtained by placing the cell under observation in the light of filters. The cell was placed in a photometer and Wratten[7] light filters of various colors placed between the cell and a light source consisting of a 100-watt lamp. These filters were previously calibrated with the aid of a thermopile.

When the cell is being used the temperature should be kept below 45° C., since above this temperature the electrolyte is decomposed into a basic copper formate,[8] which precipitates upon the plates and decreases their action. Fig. 3 shows the variations

of the output of the cell with temperature. A maximum action is produced at about 38° C. At low temperatures the electrolyte does not readily form a deposit upon the plates. At higher temperatures the character of the deposit and the electrolyte is changed.

As this light cell did not show any appreciable induction or deduction period, the author constructed what might be termed a light alternating current generator, in order better to study the ultimate action of the cell.

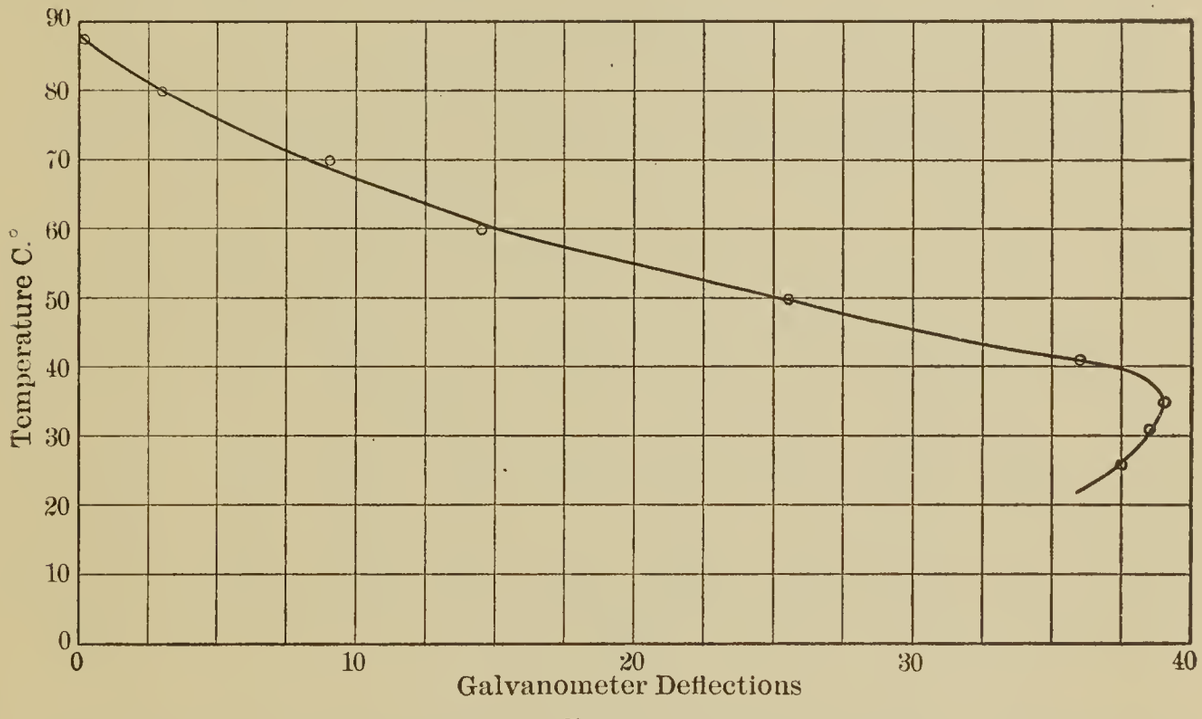


FIG. 3.

THE ALTERNATING CURRENT CUPROUS OXIDE CELL.

The cell described above was mounted between two circular disks 24 inches (60 cm.) in diameter. These disks, each of which contained six equidistant sectorial openings, were fastened to a common shaft, and arranged so that, when lights were placed outside of the disks, the openings allowed light to fall only upon one side of the cell at a time. The cell was illuminated with two 600-watt daylight lamps, arranged just outside the disks, and the light concentrated upon the cell by the aid of parabolic aluminum reflectors. The disks were driven by a variable speed electric motor, which will easily produce a light change of 120 cycles. Under these conditions the cell will produce a continuous alternating current. Receivers were connected in series with the

cell, and a clear loud note was audible. The pitch and intensity of this note varied directly with the frequency of the light interruptions and the light intensity respectively. Such a cell has been kept running continuously for a period of five hundred hours without any noticeable disintegration of the light-active material.

In order to show that the electrodes of the cell were not disintegrating, a small cell was made of electrodes one inch in diameter. The backs and edges of the electrodes were painted with a resistant enamel, and the exposed surface cleaned and highly polished. This cell was placed in a machine similar to the one described above, and the light concentrated upon the electrodes with reflectors and condensing lenses. Two No. 45 Wratten filters were inserted in the light beams to cut out as many of the heat rays

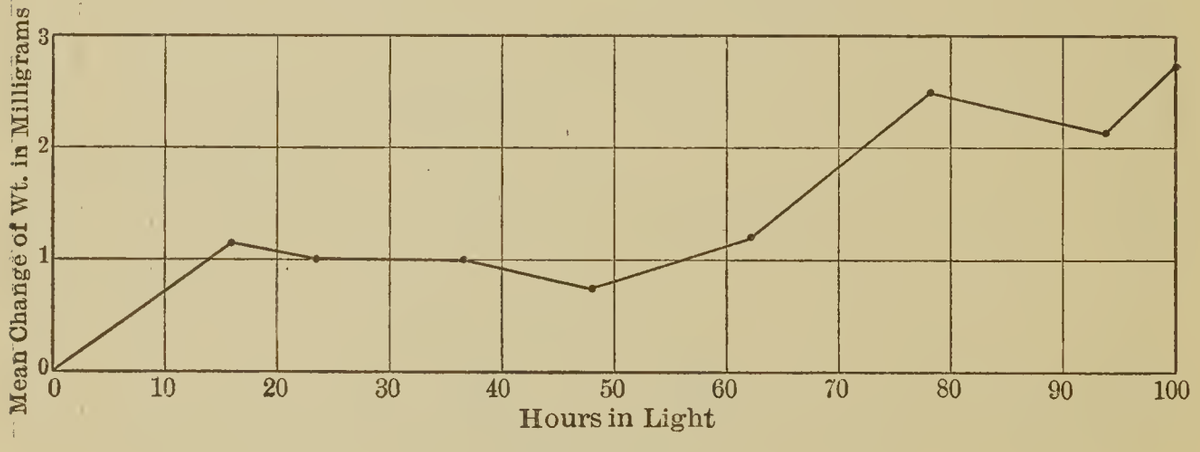


FIG. 4.

as possible. This cell was run continuously for 100 hours, and the plates weighed at intervals of about 10 hours. The curve on Fig. 4 shows there is very little change in the weight of the plates during the time of the run. The slight variations as shown are probably due, first, to variation in temperature, and, second, to the fact that the concentration of the formic acid in the electrolyte was not sufficient for complete depolarization of the cupric oxide formed. This second point was demonstrated by placing the electrodes at the end of the run in a dilute sodium chloride solution with a polished copper plate, and testing their light action. This was found to be like that of a cupric oxide plate. In the cell previously mentioned, which was run over a period of six weeks, the concentration of the formic acid in the electrolyte was correct, and in this case no excess of cupric oxide remained on the electrodes. The results seem to indicate that if

the temperature be kept within the limits stated, and the cell used continuously, there should be no ultimate fatigue or consumption of the elements of this cell.

The action and adjustment of this cell are further being studied with a Duddell thermo-galvanometer. It has been found that the amplitude, frequency, and shape of the sine curve of the alternating current may be varied by variation of the frequency of the light interruptions and the intensity of the lights on either side of the generator.

THEORETICAL.

The action of the cell seems to indicate a process of oxidation of cuprous oxide to cupric oxide under the influence of light. The cupric oxide formed is dissolved by the slight excess of formic acid in the electrolyte, and copper formate results. When a polished copper plate is immersed in a copper formate solution in the dark, a coating of cuprous oxide is formed upon the plate. When this cuprous oxide is illuminated, it is oxidized to cupric oxide, the formic acid present in the solution catalyzing this reaction. This is then the oxidizable electrode, which becomes the negative plate, and a current will flow from the unexposed plate to the exposed plate in a circuit made outside the cell. Hence, the exposed plate becomes the anode and the unexposed plate the cathode. This cupric oxide is removed from the plate as fast as formed by the formic acid acting as a depolarizer, copper formate being formed, and the electrolyte being regenerated through the action of the cell itself.

$$CuO + 2HCOOH \rightleftarrows Cu(HCOO)_2 + H_2O$$

This will continue until the active material on the plate is consumed, when the current will fall to zero. Now, if this exposed plate be made the unexposed electrode, we shall have the same condition as in the beginning, namely copper in contact with a copper formate solution. A coating of cuprous oxide will be formed upon the plate, and when this is exposed to light the cycle will be repeated.

It will be noted that in each cycle of oxidation and removal of a molecule of copper oxide, one atom of copper is removed, probably, from the electrode itself. This means that the elec-

trode will lose weight. This was shown experimentally and is illustrated graphically in the curve on Fig. 5. A copper plate was carefully cleaned and weighed, and then immersed in a beaker containing two liters of 2.5 percent copper formate solution at 40° C. This plate was made the exposed plate throughout the run and short-circuited to a polished copper plate kept in the dark. The solution was constantly stirred mechanically. After standing one-half hour in the dark the front plate was removed and reweighed. This showed the amount of the deposit thrown down by the action of the electrolyte upon the plate. The plate was replaced in the solution, illuminated strongly one-half hour, and again weighed. This treatment in the dark and then in light

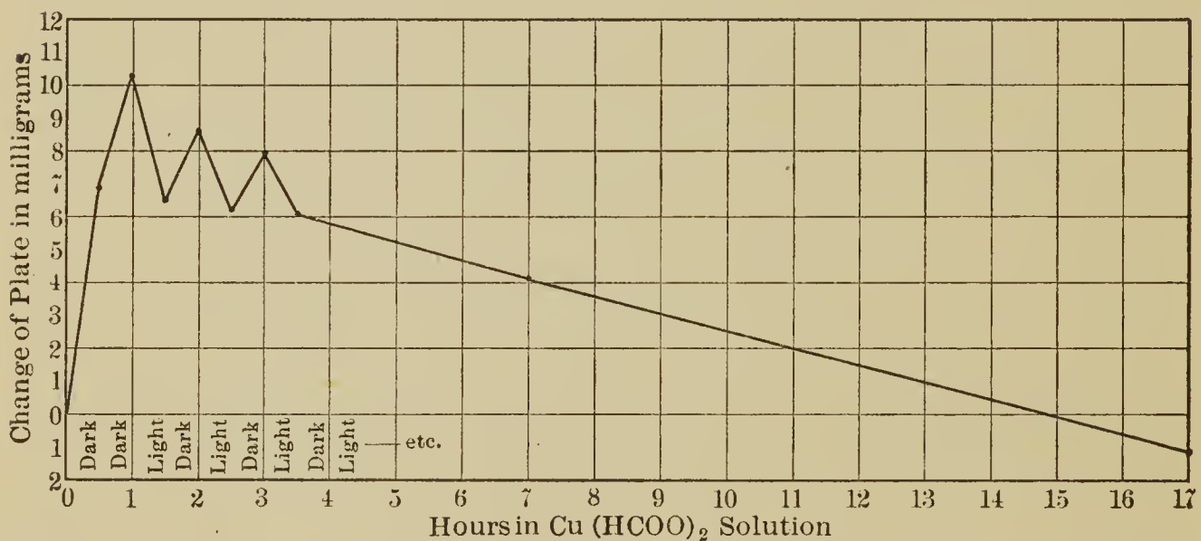


FIG. 5.

was successively repeated, and the curve shows that the plate gradually decreased in weight. The condition in the cell is similar to the above, but there are two electrodes in the electrolyte, one of which is the cathode. If the electrolytic action of the current flowing be taken into account, theoretically there should be copper plated out on the cathode which would compensate for the loss of copper on the illuminated anode plate; providing no side reactions interfered, and providing the efficiency of the cell were a maximum. The curve in Fig. 4 tends to illustrate this. In carrying this out experimentally, air should entirely be eliminated from the electrolyte in order to cut down oxidation from this source. The author, however, has not had time to carry out this phase of the question.

The observed voltage of the cell does not agree with that calculated for the oxidation of cuprous oxide to cupric oxide on the basis of Thomson's formula:

$$E_{volts} = z\ H\ J$$

where E is the electromotive force;
z the electrochemical equivalent, in grams per coulomb;
H the heat of the reaction, per gram of metal;
J the joules equivalent to 1 calorie.

$Cu_2 + O \rightleftarrows Cu_2O + 332.5$ cal.[9] per gram copper.
$Cu + O \rightleftarrows CuO + 585$ cal. per gram copper.
E_{volts} for oxidizing Cu_2O to $CuO = 0.696$ volt.

The reasons why the calculated and the observed voltage do not agree offer a very good ground for discussion.

When running this cell to produce an alternating current in the apparatus described above, the voltage obtained is higher than before obtained. This may be a polarization effect due to the cupric oxide not being removed as fast as formed. If cupric oxide be formed in the light and then an instant later be made the unexposed plate, it will tend to produce an E. M. F. of the same sign as that produced by the cell, and so increase the voltage.

The oxidation theory given above is further borne out by the following experiments: Some pure cuprous oxide was prepared by reducing a solution of copper sulphate with an organic reducing agent. The cuprous oxide so prepared showed practically no divalent copper as indicated by the fact that it formed a colorless solution with ammonium hydroxide. Some of this oxide was mixed with very dilute formic acid (0.5 percent) to form paste. This paste was spread upon a filter paper and exposed a few seconds to sunlight. The red color changed at once to a deep red and then black, and the resulting substance showed the presence of divalent copper. This would indicate that the cuprous oxide in the presence of formic acid in light is oxidized to cupric oxide.

$$Cu_2O + O \rightleftarrows 2CuO$$

This action is not nearly so noticeable when the cuprous oxide is moistened with distilled water instead of formic acid. The cupric oxide will dissolve in formic acid forming copper formate.

$$CuO + 2HCOOH \rightleftarrows Cu(HCOO)_2 + H_2O$$

It may be noted here that cuprite (Cu_2O) darkens when exposed to ultra-violet light, its change of resistance action is lessened, and its fatigue enormous. In this case the cuprite under the influence of light may be thrown into a state of tendency to oxidation, which may be a cause, or perhaps only an attendant state in its change of resistance. In the work with the ultra-violet light considerable ozone was formed. This might have helped to satisfy the greater tendency present in the cuprite due to the influence of such short wave lengths. The facts in this instance have not yet been determined. On the other hand, the cupric oxide forms a very sensitive photo-chemical cell, but the author has had no success in finding any resistance change in tenorite (crystallized mineral CuO) under the influence of light. What is the ultimate physical cause of the action of light on the cuprous oxide of the cell? The author does not pretend to know. It may be due to the liberation or rearrangement of the so-called valency electrons in the structure of the reacting substance, which would then cause a change to take place resulting in a chemical reaction, an oxidation in this case.

It may be interesting here to comment on the oxides and their appearance on copper plates which have been heated. A copper plate may be heated in such a manner that the coating formed appears quite red, and would, to all outward appearances on account of the color, be taken for a purely cuprous oxide coating. The author was at first misled by this appearance more than once. The results of experiments, however, show that this red coloration cannot be treated as a cuprous oxide in the light-action phenomena, as a burned plate was never obtained which gave a characteristic cuprous oxide light-reaction in a sodium chloride solution, no matter what the appearance of its color. In fact, the best cupric oxide coating for light reaction the author ever had, was of the most intense red color. It must have been cupric oxide which was reacting as this plate upon illumination became cathode. In other words, a reduction was taking place, which could not

have been the case if it were a cuprous oxide in either a copper formate or sodium chloride solution, in which solutions cuprous oxide changes toward the higher oxide. The color, then, of a burned plate, means nothing in regard to the oxides present. If there be any cuprous oxide present on a burned plate, its action is always blanketed by the surface film of cupric oxide, although not manifesting itself in a black color. This is probably why the action of cuprous oxide in light has so long been overlooked.

SUMMARY.

1. A method and apparatus has been described for the search of new reactions in the Becquerel E. M. F. effect.

2. A cell, copper | cuprous oxide | aq. copper formate + formic acid | cuprous oxide | copper, has been described; and its action studied.

3. This cell has been arranged to give alternating current of various amplitudes and frequencies.

4. The action of this cell indicates that, under proper conditions, its life may be continuous and its elements will not disintegrate.

5. The action of this cuprous oxide cell is compared with the change of resistance effect of the mineral cuprite (Cu_2O).

6. The contrast between the E. M. F. effect of cuprous oxide and cupric oxide is discussed.

7. The action of the cuprous oxide photo-chemical cell is explained on the basis of the oxidation of cuprous oxide to cupric oxide in light.

8. It is shown that there is no relation between the sign of the light action and the color of heated copper plates.

REFERENCE NOTES.

1. E. Becquerel, Diss. 1840, Die chemischen und elektrischen Wirkungen unter Einfluss des Sonnenlichts.
Ann. d. Ph. e.d. Ch. (1843), **9**, 268.
Ann. d. Ph. e.d. Ch. (1851), **32**, 176.
Ann. d. Ph. e.d. Ch. (1859), **56**, 99.
La Lumiere, ses Causes et ses Effets (1868), **2**, 121.

2. Minchin, Phil. Mag. (1891), **31**, 207.

3. See Kochen, Jahre d. Radio-aktivit u. Elektron (1905), **2**, 186.

4. Wildermann, Proc. Roy. Soc. (1905), **74**, 369.
5. Miller, J. Phy. Chem. (1916), **13**, 256.
6. Pfund, Phy. Rev. (1916), **7**, 289.
7. See absorption curves, Wratten Filters, 1916.
8. Ribau, Bull. Soc. Chim. (1882) [**2**] **38**, 112.
9. From Smithsonian Tables.

Case Research Laboratory,
Auburn, N. Y.

DISCUSSION.

C. G. FINK[1]: I would like to ask Mr. Case to try out other metals and other oxides, some of which may have a much stronger photo-chemical effect than copper oxide. For example, tungsten oxide exposed to light is readily reduced to a blue oxide, and, as is well known, silver oxide is also affected by light. It does seem to me that the experiments Mr. Case has conducted will eventually lead to valuable practical applications.

W. R. MOTT[2]: The production of the blue oxide from the tungstic oxide by action of light is an experiment that I carried out several times. The method I used was to place the oxide on top of mercury in a test tube, inverted in a mercury trough; then, with a lens, to concentrate the light of the sun, or of a powerful artificial light, such as the flame arc, on the oxide for some hours and in that way get several cc. of oxygen from the WO_3. Tungstic oxide (WO_3) was first decomposed by light by Sir Humphrey Davy, in his first attempts to find the relation of heat and of electricity to chemistry.

T. W. CASE: In reply to Mr. C. G. Fink, I will try out other metals and their salts as soon as conditions permit.

[1] Research Chemist, Edison Lamp Works, Harrison, N. J.
[2] Research Laboratory, National Carbon Co., Cleveland.

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 4, 1917, President FitzGerald in the Chair.

CHEMISTRY OF THE FLAMING ARC, IN RELATION TO LUMINESCENCE.

By Wm. Roy Mott.

[*Abstract.*]

1. Introduction.
2. Comparison of Carbon Arc and Flaming Arc.
3. Magnified Arc Image: Apparatus and Method.
4. Color of Arc Parts of nearly all Elements.
5. Divided and Diffused Negative Craters.
6. Volatility and Crater Distance.
7. Materials Less Volatile than Carbon. Pitting Residues.
8. Typical Characteristics for Analytical Purposes.
9. Four Light Sources due to reactions with Calcium Fluoride in Arc.
10. Effect of Alkali Salts on Cyanogen Bands.
11. Results from the Electrochemical Standpoint.
12. Conclusions.

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1. Introduction.

The line and band spectra of the flaming arc prove that the vapor form of elements and certain compounds is the source of the light of the arc stream. This arc stream usually consists of two differently colored parts. The core probably gives light by electro-luminescence and the outer shell by chemi-luminescence. The arc parts are best seen by the beautiful projected arc images obtained on the principle of "the camera lucida." (Moissan used this but slightly, as he wished to avoid the electrolytic effects of cratering. See page 32, Lenher's translation, The Electric Furnace.) I believe my results will be of special interest to the electric furnace industry as well as to the art of most efficient light production. (Extraordinary efficiencies of flaming arcs were recently measured by Dr. E. Karrer, J. Franklin Inst., Jan., 1917,

page 61.) Also new quick methods of qualitative chemical analysis have been obtained in my studies of magnified arc images and new data on relative volatility of refractory materials.

2. Comparison of Carbon Arc and Flaming Arc.

An arc is a column of very hot and highly conducting vapors carrying a current (direct or alternating) sustaining this condition. A carbon arc with light giving chemicals is called a flaming arc. The inner vapors of a carbon arc are carbon, cyanogen, and carbon monoxide, which all burn up with very little light production at the arc edges. Hence, the carbon arc wastes much energy which is efficiently utilized by the special chemicals in the flaming arc to give light of the desired color. Also, most flame chemicals better utilize the electrical energy of the arc core. The result with the flaming arc is that about 90 percent of the light comes from the arc stream and 10 percent from the craters. The exact reverse is the case with the carbon arc.

With the yellow flame arcs most of the light is produced in an outer very bright yellow shell, which on alternating current has good light giving powers (50 to 75 percent of maximum light) even at zero instantaneous current. The ordinary carbon arc gave only 10 percent of its maximum as current crossed zero. (See curves in article by C. D. Child, The Physical Review, Jan. 1917, **9**, 1.)

The flame arc like the ordinary carbon arc has a movement of material from positive to negative. This is proved by using an upper positive flame carbon with a pure carbon lower. The arc image shows full arc brightness at the negative and this electrode has a precipitation of flame material on or near the negative crater. If the polarity of this combination is reversed no flame material now reaches the lower as positive, and so the arc is essentially a pure carbon arc except for a *very short distance* out of the flame upper negative.

The flame materials give many electrical advantages to the carbon arc, such as favorable operation at very low or very high arc voltages, wide ranges of current, better power factor and far less flicker, especially on alternating current. (See writer's paper, Journal Cleveland Engineering Society (1917), **9**, 281 *et seq.*)

3. Magnified Arc Image: Apparatus and Method.

Fig. 1 shows the essential apparatus used for observing the magnified (20 diameters) arc image. This consisted of a 25 ampere (60 arc volts) Helios photo-engraving lamp, with its reflector closed with an iron disc 1½ in. (4 cm.) from the arc, protected and held in place with plaster of paris and carbon dust. This cast, on shrinking, was recemented with water glass and carbon dust. The center of the disc had a pin hole 1/64 in. (½ mm.) diameter. A lens 2 in. (5 cm.) diameter outside this aids in getting a better image. An adjustable metal box covered

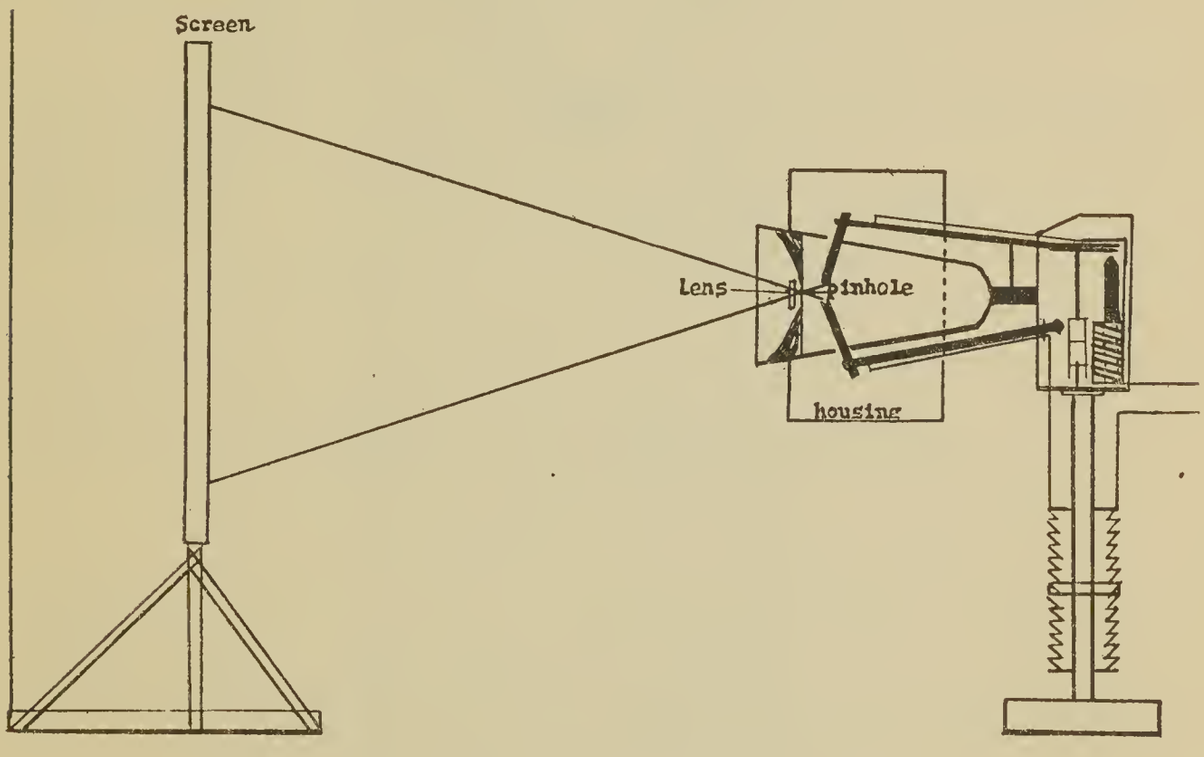

FIG. 1. Apparatus used in magnified arc image work.

the upper electrode opening; and at times this was supplemented with a black cloth. (An ordinary shunt connected lamp in a metal box can easily be used for this work.)

The observations were made in a darkened room, and the image parts were measured with a flat steel rule. A white screen received the image, which, by the way, could easily be photographed direct by sensitive paper on the screen. The images can be made large for lecture demonstrations.

Fig. 2 shows the size and shape of cup used. This was of high grade solid carbon ½ in. (13 mm.) diameter and drilled ⅜ in. (10 mm.) wide and deep. The upper was a regular solid ½ in.

(13 mm.) carbon. Graphite cup took two or three times longer to volatilize calcium fluoride than high-grade carbon. The graphite conducts the heat to the carbon holder. The flaming materials weighed (0.2 to 0.5 g.) and in powder form were usually packed in the cup. An experiment would then usually take 10 to 30 minutes to volatilize the material. Fractions of a milligram of

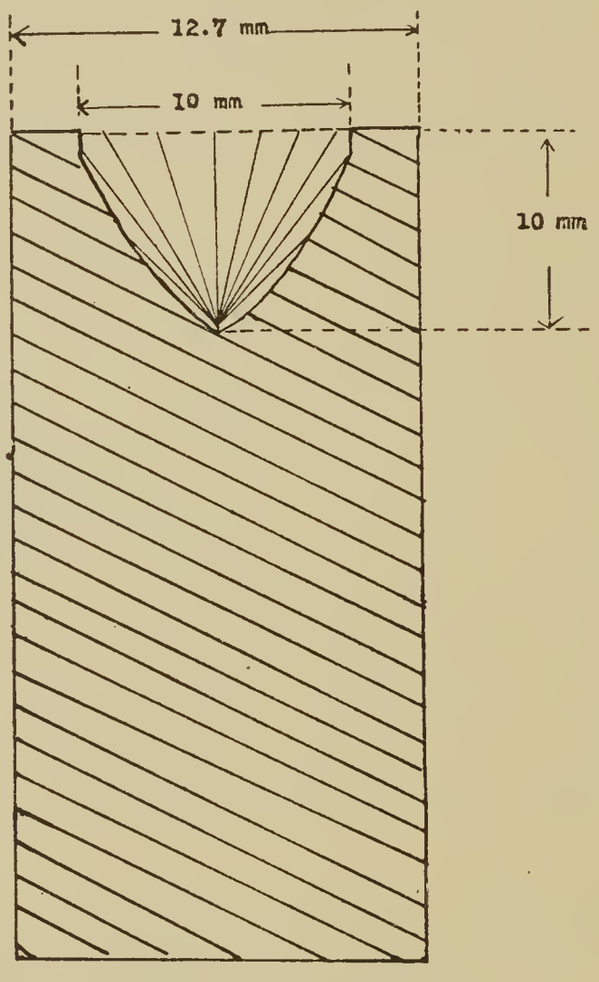

FIG. 2. Carbon cup used in experiments on magnified arc image.

some materials could easily be identified. For example—a mix with 0.10 mg. of calcium fluoride (in the bottom of this cup) started flaming in about 10 seconds after turning on the current (25 A.) and then flamed for over two seconds with a bright full yellow shell.

A good hand spectroscope was used to observe spectra of arc parts and change of spectra with mixes. Spectrum photographs (some 500) were taken with a large concave grating spectroscope of six-foot focal length.

4. Color of Arc Parts of Nearly All Elements.

The color of arc core and shell (also thickness in inches at ½ in. (13 mm.) above lower positive) was observed of materials containing nearly all elements with a 25 ampere arc. The best insight into the data is given by arranging according to the periodic law. The easily reduced elements (belong chiefly to minor sub-groups) are given first, as they show no luminous colored shell because so little energy is produced in their chemical reactions at the arc edges.

CLASS A. MINOR SUB-GROUPS; LUMINOUS COLORED CORE ONLY.

Group I.

Copper: green.
Silver: green.
Gold: green.

Group II.

Zinc: blue.
Cadmium: bluish green.
Mercury: greenish blue.

Group III.

Gallium: no data.
Indium: violet.
Thallium: intense grass green.

Group IV.

Germanium: no data.
Tin: dim faint green.
Lead: bluish green.

Group V.

Arsenic: no light except carbon arc.
Antimony: dim blue.
Bismuth: blue.

Group VI.

Selenium: no data.
Tellurium: dim blue green.

Group VII.

Bromine: no light except carbon arc.
Iodine: no light except carbon arc.

CLASS B. MAJOR SUB-GROUPS: LUMINOUS COLORED SHELL ALSO.

Group I. Valence 1. Alkali Metal Materials.

Give at the start apparently a single colored arc like Class A, but at the end with very little flame material, a fan-shaped shell structure develops at the negative: lithium blue core—red shell (0.20 in. (5mm.) thick); sodium *very dim* green core (lengthwise of arc) and yellow shell (0.16 in. (4 mm.) thick), while potassium,

rubidium and caesium have such dim grayish arcs that the arc parts can hardly be distinguished—a violet core and greenish gray shell is common to all three. With rubidium, more yellow shell as per corresponding bunsen gas flame. However, these three similar alkali elements give unique very dim repellent negative arc streams, but very bright positive arc streams with mixes containing for example equal parts of calcium fluoride and alkali sulphates (K_2SO_4.$RbSO_4$ and $CsSO_4$). Fluorides give the same spectra as other salts.

Group II. Results with Alkaline Earth Oxides.

Beryllium: violet core, dark space 0.10 in. (2.5 mm.), green shell 0.06 in. (1.5 mm.).

Magnesium: solid green, at end blue core, vague green shell.

(Oldenberg (ref. sec. 9 this paper) has shown a marked difference in magnesium oxide spectrum bands in different layers of carbon arc.)

Calcium: violet core (H & K lines), yellow shell, 0.07 in. (2 mm.)

Strontium: bright blue core, red shell, 0.07 in. (2 mm.)

Barium: reddish purple core, green shell, 0.04 in. (1 mm.)

Radium: no data; probably red shell as in bunsen flame.

Group III. Alkaline Earth Fluorides.

Magnesium fluoride: essentially same result as with oxide.

Calcium fluoride: violet core, yellow shell, 0.07 in. (2 mm.), slightly more red outer part.

Strontium fluoride: bright blue core, yellowish red shell, 0.07 in. (2 mm.) slightly more red outer part.

Barium fluoride: reddish purple core, green shell, 0.04 in. (1 mm.) spectra unlike oxide.

The chloride of barium is bright in its compound spectra. It is important to note that alkaline earth sub-halogens are of increasing stability at high temperatures, and this probably enters into the reactions causing these peculiar compound spectra.

Group III (a). Oxides and Fluorides.

Boron: violet core, dark space, 0.10 in. (2.5 mm.), green shell, 0.07 in. (1.8 mm.)

Aluminium: violet core, dark space, 0.08 in. (2 mm.), green shell, 0.06 in. (1.5 mm.)

Scandium: no tests, probably blue core, red shell.

Yttrium: intense blue core, intense red shell, 0.05 in. (1.3 mm.). The latter is replaced with green shell when arc craters entirely on oxide bead.

Lanthanum: blue core, dark space, 0.05 in. (1.3 mm.), yellow green shell, 0.05 in. (1.3 mm.). This is unique in having a bright blue core and dark space.

Group IV. Valence lower than four (except for Thorium).

Carbon: violet core, no shell.

Silicon: bluish violet core, very dim green shell, 0.12 in. (3 mm.)

Titanium: intense blue core, greenish yellow shell, 0.04 in. (1 mm.) Unique in giving a deep green shell with chromium.

Zirconium oxide or fluoride: intense blue core, yellow white shell 0.07 in. (1.8 mm.), which seems to be due to a continuous spectrum of solids condensing and reacting in outer arc parts. Zirconium carbide is less volatile than platinum.

Cerium: intense blue core, dim yellow shell, 0.07 in. (1.8 mm.)

Thorium: blue core, yellow red shell, 0.01 in. (0.25 mm.) With thorium oxide having crater on same there is a thick yellow white shell with red edges—probably due to continuous spectra of solid oxide which has probably the highest boiling point of any known oxide.

Group V. Maximum Valence of Oxidation Five.

(These show marked stability at lower valencies, and some double colored shells.)

Nitrogen: non-metallic element, no light except as CN or BN.

Phosphorus: nearly non-metallic element, no light and only four far ultra-violet lines in carbon arc; phosphates, dim arcs and craters.

Vanadium: reddish purple core, yellow green shell, 0.03 in. (0.8 mm.) Easily recognized.

Columbium: blue core, yellow green shell, 0.05 in. (1.3 mm.), *red edge,* 0.01 in. (0.25 mm.)

Tantalum: blue core, blue green inner, 0.15 in. (3.8 mm.), *reddish yellow outer,* 0.05 in. (1.3 mm.)

Group VI. Some Multi-colored Shells.

Oxygen: non-metallic, no element lines, numerous compound spectra.

Sulphur: no light as element or compound in carbon arc, so far as known.

Chromium: blue green core, greenish yellow shell, 0.05 in. (1.3 mm.) (Deep green shell with titanium.)

Molybdenum: blue core, green shell, 0.10 in. (2.5 mm.), faint red outer edge, 0.02 in. (0.5 mm.)

Neodymium: blue core, green inner, reddish outer, all shell, 0.06 in. (1.5 mm.)

Tungsten: blue violet core, faint green shell, 0.12 in. (3 mm.).

Uranium: intense blue core, green inner shell, 0.05 in. (1.3 mm.), faint red outer, 0.05 in. (1.3 mm.) The total light is a bluish white, with the most near and far ultra-violet of any known material.

Group VII.

Fluorine: as element, no light, but beautiful bright compound spectra with BeF_2, CaF_2, SrF_2, and BaF_2. CaO very sensitive test for fluorine materials.

Chlorine: as element no light, but peculiar compound spectra, as with fluorides. Barium chloride appears brightest of these in arc.

Manganese: blue core, yellow green shell, 0.11 in. (3 mm.)

Group VIII. The Magnetic Elements.

Iron: intense blue core, bright yellow shell, 0.07 in. (1.8 mm.)

Cobalt: blue core, reddish yellow shell, 0.10 in. (2.5 mm.)

Nickel: greenish blue core, dim yellow shell, 0.15 in. (4 mm.)

Platinum: (with 10 percent iridium) blue core with a tendency to a vague greenish shell. (Marked precipitation of bright platinum as small beads at edge of negative crater.)

5. Divided and Diffused Negative Craters.

The negative crater derives its energy in a carbon arc from the hot vapors from the positive. With two half-electrodes having even adjacent small points, the negative crater seeks the one of least heat conductivity. For example, high-grade carbon will hold the negative crater from graphite until a marked difference in heights of points is seen. The reverse is the case with the positive crater which is pulled to the graphite by its flaming impurities. It is a striking experiment to divide the negative crater by inserting between two small high grade electrodes, as above, a thin graphite plate, then the *negative crater can be divided on the two high-grade carbons.* With some flaming materials, divided positive and negative craters are still more easily obtained.

Very dim large negative craters are most easily produced by volatilizing barium salts from the positive cup. The formation is preceded by a blue or purple luminescent dim ring around the intensely bright negative, which changes shape and disappears gradually into a large, uniformly dim negative crater.

Average Diameters of Large Dim Negative Craters after volatilizing 0.2 gr. of oxide.

Ba	0.30 in. (7.5 mm.)	Ce	0.25 in. (6.3 mm.)
Sr	0.23 in. (6.0 mm.)	Zr (slow to form)	0.22 in. (5.5 mm.)
Ca	0.17 in. (4.3 mm.)	Ti (slow to form)	0.17 in. (4.3 mm.)
La	0.20 in. (5 mm.)	Ta	0.22 in. (5.5 mm.)
Yt*	0.17 in. (4.3 mm.)	Cb (not marked)	0.13 in. (3.3 mm.)
Th	0.22 in. (5.5 mm.)	V (not marked)	0.13 in. (3.3 mm.)

* Yttrium gave a dim ring, but its center held an intensely bright spot. The carbon arc gave a negative crater about 0.11 in. (2.8 mm.) under like conditions (25 A). The alkali salts, beryllium, magnesium, boron, aluminum, silicon, chromium, manganese, iron, nickel, cobalt, platinum do not give diffused negative craters, whose formation no doubt depends on intense nitrogen—carbon reactions with elements giving diffused negative; for example, barium no doubt gives cyanide, and calcium, cyanamide.

6. Volatility and Crater Distance.

The crater distance (or distance from the crater to the molten material) appears to depend chiefly on the heat conductivity of the carbon material and the boiling point of the material in the carbon cup. This applies especially to fluorides which do not allow the arc to crater from them. Materials allowing cratering are rapidly volatilized. Using very small metal beads (0.2 to 0.5 gr.) of copper silver, lead and bismuth (these do not dissolve

carbon* or fluoride) and small amounts of fluorides, and weighing separate beads after heating in crater for measured time, gave the following order of volatility (least volatile first) Cu, Ag, SrF_2, CaF_2, BaF_2, Bi, LiF. This, with crater distance data, enabled approximate boiling point to be calculated.

Average Crater Distance with High Grade Carbon (Hardness 5.0).

Least Volatile Fluorides.	Limits Shortest Steady Distance.	Average.
Strontium Fluoride	0.01 to 0.03 in. (0.25 to 0.75 mm.)	0.02 in. (0.5 mm.)
Calcium Fluoride	0.025 to 0.033 in. (0.65 to 0.85 mm.)	0.03 in. (0.8 mm.)
Rare Earth Fluorides	0.02 to 0.04 in. (0.5 to 1 mm.)	0.03 in. (0.8 mm.)
Barium Fluoride	0.05 to 0.08 in. (1.3 to 2 mm.)	0.06 in. (1.5 mm.)
Sodium Fluoride	0.05 to 0.08 in. (1.3 to 2 mm.)	0.07 in. (1.8 mm.)
Lithium Fluoride	0.06 to 0.09 in. (1.5 to 2.3 mm.)	0.10 in. (2.5 mm.)
Potassium Fluoride	0.07 to 0.14 in. (1.8 to 3.6 mm.)	0.10 in. (2.5 mm.)
Cadmium Fluoride	0.07 to 0.13 in. (1.8 to 3.3 mm.)	0.10 in. (2.5 mm.)
Chromic Fluoride	0.10 to 0.15 in. (2.5 to 3.8 mm.)	0.12 in. (3 mm.)
Aluminum Fluoride	0.10 to 0.13 in. (2.5 to 3.3 mm.)	0.12 in. (3 mm.)
Zirconium Fluoride	0.16 to 0.26 in. (4 to 6.6 mm.)	0.20 in. (5 mm.)

The time to volatilize equal weights followed this general order except for the fluorides which wet carbon, namely KF, BaF_2 and NaF. Without going into further detail, the boiling point figures are probably within 50° of the true value at 760 mm.

	Estimated Normal Boiling Point
Strontium Fluoride	1900° C.
Calcium Fluoride	1800° C.
Barium Fluoride	1400° C.
Lithium Fluoride	1300° C.

Some of the rare earth fluoride mixtures seemed to have a slightly higher boiling point than silver (1955° C. Greenwood†) but decidedly less than that of copper.

7. Materials Less Volatile than Carbon: Pitting Residues.

The following give residues less volatile than iron or carbon, and, except vanadium, less volatile than platinum, when mixes were fractionally distilled. The time required to volatilize is of less significance than fractionally distilling, if the final product is practically freed from others. V distilled from Mo. All distilled from tungsten.

* (Moissan (Compt. Rend. (1896), **122**, 1462) says Au, Bi, Sn do not dissolve carbon, Au dissolves only "une très petite quantite," and Ag dissolves "une petite quantite.")

† (H. C. Greenwood, Proc. Roy. Soc. London (A) **83**, 483-92.)

Time to Volatilize.

Vanadium	0.15 g.	20 min.
Molybdenum	0.20 g.	33 min.
Molybdenum	0 40 g.	60 min.
Columbite	0.20 g.	30 min.
Tantalite	0.20 g.	31 min.
Barium tungstate	0.50 g.	300 min.

The barium part distilled in a few minutes of course. By careful co-ordination of crater distance, time to volatilize, extent of cratering, brightness of crater, and distilling mixes, the approximate boiling point of these and other metals, etc., in the carbon cup can be determined. As aid in this, delicate chemical tests are desirable.

8. Typical Characteristics for Analytical Purposes.

By the magnified arc image, good tests can be found for nearly every element, even in the presence of all others. There is probably no property more efficient for separation than boiling points, which extend over enormous ranges. A complete description of detailed tests naturally belongs to another paper which I hope to publish shortly. The outline below, however, summarizes group characteristics in their general order of separation on a volatility basis.

Class A: Give an arc stream with no colored shell, and the metal forms beads not wetting or dissolving carbon. The color of arc, metal, and deposits readily allow recognition. Cd (red upper), Zn, In, Sb (white upper), Bi (yellow edge upper), Tl, Pb, Ag, Sn, Cu (red cut metal), Au (purple upper).

Class B: Arc gives differently colored parts. If metal residue, it wets carbon in irregular melts. Groups depart from periodic set so as to be in order of volatility of residue formed in cup starting with oxycompounds.

Group I. Alkali: Solid color at start; Li, at end of experiment a fan-like red shell near negative; Na, yellow, lengthwise color difference in arc stream with K, Rb, Cs, long dim arcs.

Group II. Alkaline earth: Negative deposit, oxidized in cooling, and so gives only alkaline reaction with water. Fluoride

spectra different from oxide except for Mg, which gives only vague shell.

Group III. Elements near boron: Nearly carbon arc core, dark space, green shell; B, black glaze upper; Al, popping oxide bead; BeO, least volatile of all non-cratering oxides; Si, no dark space but dim arc.

Group IV. Rare earths: Unique in giving carbide deposit (in negative crater) which on cooling and adding water swells and gives acetylene odor. Arc will crater on oxides.

Group V. Iron-like metals, Mn, Co, Ni, Fe, Cr, give irregular metal melt wetting and dissolving carbon. Arc craters dimly on melt, and negative crater normal in size and brightness.

Group VI. Metals like group V but oxides and carbides like Group VII. Ti, brown oxide, diffused negative; Zr, arc colors; ThO_2, non-volatility, etc. (Thorium very short arc at times.)

Group VII. Elements and carbides most refractory. Intermittent carbon arc. Fractions of a milligram easily tested.

Vanadium: unique arc colors, unique yellow green deposit on upper.

Uranium: three colors in arc, scintillating sparks, colored upper.

Platinum: characteristic small bright metal beads, negative tip.

Molybdenum: bluish mirror metal pits.

Tungsten: least volatile of all, fraction of a milligram, dim pool in positive crater, cold carbon yellow (WO_3), white hot carbon gives a garlic odor, very good test, no odor from other members of this group.

9. Four Light Sources due to Reactions of Calcium Fluoride in Arc.

The spectrum photographs (6500 A. to 1700 A.) with the alkaline earth fluorides gave all the bands and lines given by the corresponding carbonates, except for new green, yellow and red bands and no change in blue, violet or ultra-violet. (The spectrum of fluorides is not different from the corresponding oxycompounds with alkali elements or rare earths.) The calcium fluoride arc was observed also in natural gas, carbon dioxide and in free

chlorine, giving results showing that nitrogen gave essentially no effect on the spectra while oxygen was important. *Calcium fluoride bands were very bright in arc shell* and extended further (lower boiling point than oxide) in hot vapors above the arc, as would be predicted from calcium fluoride bands being easily producible in an ordinary hot blast flame. They are the *only bands* or lines (except sodium impurity) that I have caused to suffer reversal with a yellow flame arc under conditions favoring great excess of calcium fluoride vapor—such as short, shielded arcs or arcs under water or paraffine. With the arc under water the enlarged arc image showed a narrow arc with a thin shell, but near the upper electrode there was a globular vapor feed from one point in the arc and giving the band spectra due to the chemical reactions which might be as follows:

$$2CaF_2 + C \leftrightarrows 2CaF + CF_2$$
$$CaF + CNF \leftrightarrows CaF_2 + CN$$
$$2CaF + CF_2 + O_2 = 2CaF_2 + CO_2$$
$$2CN = C_2 + N_2$$
$$2CN + 2O_2 = 2CO_2 + N_2$$

Reversal of the alkaline earth fluoride bands has also been obtained by flashes, by W. J. Humphreys (Astrophysical Journal (1905) **22**, 220.) *Calcium oxide bands* are also only given in the outer shell of the calcium fluoride arc, and give perhaps about one-third the total light using oxide spectra and using data on energy spectrum distribution of fluorides by Jaschke. (Book "Specktro-photometrische Untersuchungen, etc." published at Breslau by H. Fleischmann, 1904.) *Calcium carbide* gives some green bands especially near the negative electrode. Olmsted (Astrophys. J. (1908) **27**, 66-69) noted "beautiful green bands degraded toward the red" with an arc on calcium carbide. *Elemental calcium lines* give the core of all arcs with calcium salts a violet color due to H and K lines which A. S. King (Astrophys. J. (June, 1909) **29**) showed do not appear below 2500° C. in his tube furnace. The low temperature calcium line at 4227 A. was observed in arc shell in the beautiful research on arc structure by Oldenberg (Zeitschrift für wiss. Photographie, etc. (1913) **13**, 133.)

10. Effect of Alkali Salts on Cyanogen Bands.

The cyanogen bands are greatly diminished in intensity by alkali and alkaline earth fluorides; KF most, then in order NaF, BaF_2, SrF_2, CaF_2. This is also shown by a marked decrease in photographic power of the arc as a whole on solio paper. From this and the power of potassium fluoride to give longest arcs, I suggest the following reaction as explanatory of decreased cyanogen band and marked arc conductivity: $KF + 2CN = KCN + CNF$. These materials would oxidize at arc edges through cyanate (KCNO) and finally back to potassium fluoride (KF), carbon dioxide (CO_2), and free nitrogen. Thermal data on heats of reaction favor above theory, as well as similarity of potassium, rubidium and caesium in chemical reactions, in giving very long arcs, and in giving large dim diffused positive craters.

In collecting a large number of beads of calcium fluoride after fusing in a carbon cup, I obtained on storing these, in a clean closed bottle after a few days, a decided odor of cyanogen; verified further by duplicate tests and several persons observing the odor. This is the only occasion I know of cyanogen being removed from the arc, although there is considerable literature on the preparation of hydrocyanic acid (HCN) with carbon arcs in hydrogen and hydrocarbon vapors.

11. Results from the Electrochemical Standpoint.

From an electrochemical standpoint the arc has considerable analogy to an electrolytic cell: First, the anode material moves to the cathode. Second, the anode heat is probably due to a transfer high resistance layer (similar to aluminum anode in rectifying solution.) Third, the anode need not dissolve, if other more easily attacked material is available. Fourth, the most electropositive elements, especially those with two or more high temperature valences (CaF, CaF_2, for example) tend to give a bright arc shell due to chemi-luminescence. Fifth, the electronegative (non-metallic elements) do not give light in carbon arc as elements but may do so as compounds.

12. Conclusions.

1. There is no case of a blue arc shell.
2. In every case except Ba and V, the arc core is blue or violet

and the shell green, yellow or red. Hence the hue of shell in every case except Ba and V is of a longer wave length than hue of arc core.

3. All the non-metallic elements (F, Cl, Br, I, O, S, N) give no elemental spectra, but F, Cl, O, N give some compound spectra in a carbon arc, such as the halogens with alkaline earths except Mg, many oxides, a few nitrides.

4. The intermediate elements, P, As, B, give no visible and only a few ultra-violet lines in the carbon arc.

5. The easily reduced metals (*i. e.*, easily electrolyzed in metallic form from aqueous solution) give no arc shell except the iron (magnetic) group of elements. The low energy of reaction at high temperatures explains this lack of light.

6. The most electropositive elements give the most marked colored luminous shells especially where more than one valence stage is characteristic of the element at high temperatures.

7. With yttrium oxide, the crater on the bead alone gives a green shell replacing the usual red, with crater partly on bead and on carbon.

8. Zirconium oxide gives a yellow-white shell. The yellow-white is probably due to hot solids, as zirconium carbide is less volatile than platinum and its oxidation would give also extremely non-volatile oxide. Zirconium metal is fairly volatile.

9. In nearly every case with a carbon arc, the flow of material is from positive to negative. However, with the salts of K, Rb and Cs, there is in mixtures with for example calcium fluoride a strong blast which also comes from the negative crater causing a unique dimness near the negative part of arc.

10. A dim, large positive crater can often be produced by nearly all salts of K, Rb, Cs and oxysalts of sodium. This with the effect on cyanogen bands and marked arc length may be explained by the reaction: $KF + 2(CN) = KCN + CNF$, and others necessary to return by oxidation to KF, CO_2 and N_2.

11. A dim negative crater is most easily produced by barium salts volatilized from the positive. This as well as that with other materials is probably connected with nitrogen reactions at fairly high temperatures.

12. Beryllium oxide is the least volatile of the oxides which are

so insulating as not to allow cratering, such as alkaline earth oxides, aluminium oxide, and silica.

13. The oxides of yttrium, zirconium, thorium and other rare earth elements allow cratering.

14. Tungsten is easily the least volatile of all known elements, with tantalum second.

15. The light sources of a yellow flame arc are due to reactions involving calcium fluoride, calcium oxide, calcium carbide and elemental calcium (lines), in addition to usual carbon arc light sources.

16. A simple cheap means of qualitative analysis is found in the magnified arc image. This enables much data on relative volatility to be quickly obtained.

I here take pleasure in thanking especially Mr. P. P. Bethea and Mr. C. F. Fellows, for able assistance in carrying out my experiments and checking observations.

Research Laboratory,
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DISCUSSION.

G. M. LITTLE[1] (*Communicated*): Mr. Wm. R. Mott's paper, "The Chemistry of the Flaming Arc, in Relation to Luminescence," is of great value to those who are investigating the light-giving properties of the elements, and a careful study of it will save them much time and labor.

Much work has been done which is narrowly confined to carbon and to the fluoride and oxides of calcium, cerium and titanium. It is gratifying to have some one who has had a large experience with these materials tell us some of the properties and limitations of the other elements.

Mr. Mott's grouping of the elements according to the periodic system makes the work much more understandable, and suggests the hope that the periodic law may be instrumental in developing the light-giving properties of the arc, as it has led to the discovery of unknown elements, the correction of atomic weights, etc.

[1] Chemist, Westinghouse Electric & Mfg. Co., Pittsburgh.

C. G. FINK[2]: Conclusion No. 14 is "Tungsten is easily the least volatile of all known elements, with tantalum second." Does Mr. Mott refer to tungsten metal?

W. R. MOTT: I refer to the actual metal, placed in the carbon cup. In the case of tungsten, this would result in formation of carbide.

C. G. FINK: Accordingly, if you mix tungsten with other metals and play the arc, tungsten is the only one left at the end, the conclusion is then, that, in the carbon cup, tungsten is the least volatile of them all. Further on Mr. Mott says that tungsten carbide was little more volatile than the metal itself. On page 375, do the "approximate boiling points" refer to the metals or their carbides?

W. R. MOTT: The boiling points refer to the metals placed in carbon cups. Being in a carbon cup would only slightly affect the boiling points of metals like silver, gold, tin, etc., which dissolve very little carbon, if any. With the iron group of metals considerable carbon is dissolved, and this raises the boiling points a few hundred degrees. See Ruff's researches on Fe, Ni, Co, Mn, etc. I have been told that tungsten carbide is more volatile than the pure metal. Zirconium is a peculiar case, as the metal particles are protected by a thin oxide film (ZrO_2). This oxide melts at about 2,500° C., and the metal much lower. This protective oxide shell delays the formation of carbide, and because of the several changes in the character of the arc the metal volatilizes first—even below the boiling point of iron, the oxide and carbide being far less volatile than iron.

C. G. FINK: I know that it is usually thought that zirconium oxide is not reducible. My experience is that zirconium oxide is easily reducible; yet in the carbon arc, you say, it is not readily reduced.

W. R. MOTT: That is essentially right, especially with oxide 99.5 percent pure. There are three elements whose oxides are very difficult to reduce, or, if reduced, to keep them so. These form in lace shapes on the tip of the negative electrode, right next to the negative crater. This lace-like formation is most

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evident with beryllium, zirconium and thorium. Beryllium oxide is apparently more difficult to reduce than any of the others. It is an extremely inert material. I think it will be one of the dominant future electric furnace materials, when it can be procured in quantity, as there are large sources of it in the New Hampshire beryl. Its purification is a problem which can be worked out. The high heat of formation of zirconium oxide suggests difficulty of reduction. Some Zr_2O_3, the yellow intermediate oxide, is sometimes obtained during reduction.

C. G. FINK: The information contained in Mr. Mott's paper ought to give rise to a dozen more papers at future meetings. It ought to stir up some of our more theoretically inclined members to interpret some of the peculiar phenomena so strikingly brought out in Mr. Mott's drawings.

W. P. MOTT: It is not at all difficult to study the groups, and you can easily take an ordinary street lamp and put a shunt around it, at a few dollars expense, and then take some ordinary enclosed arc carbons (high-grade carbons), and make the cups as described. The experiments take only a few minutes after you have the apparatus set up. You can either use a darkened room or project the arc into a darkened room, through a sheet-iron or other diaphragm. When the apparatus is set up, you can identify almost any element, without spectroscope examination, although such is desirable in some cases.

J. W. RICHARDS[3]: I was interested in the data given on pages 374 and 375, where Mr. Mott estimates the boiling points of four different fluorides, and also compares the volatility of several metals. As I understand it, he compares the times to volatilize equal weights. I think that the times to volatilize equal molecular weights are what should be compared. The energy required to volatilize molecular weights of substances is practically proportional to the temperature (absolute) of volatilization, and therefore if you want to find the temperatures which are necessary to boil these substances, or volatilize them, you should compare the relative times to volatilize equal molecular weights of the materials, and not actual weights.

Some of you probably recall the paper by Dr. Watts, in our

[3] Professor of Metallurgy, Lehigh University.

Transactions[4], in which he compared the relative volatilization temperatures of the metals, taking the experiments of Moissan as to the weights of metals volatilized in a given time in Moissan's electric furnace, and taking two arbitrary points of reference, I think the boiling point of zinc as one, and the boiling point of tungsten as the other. He thus arranged the elements in the order of their boiling points, and estimated what the actual boiling points were of these high-boiling-point metals. The error of that method was particularly that he compared the times of volatilizing equal weights, instead of equal atomic weights of the metals, at the temperatures necessary to boil them.

W. R. Mott: I appreciate the suggestion of Prof. Richards and quite agree with him we ought to use the molecular weight of the vapor, if we only knew it, but we do not; we do not know whether these are really atomic vapors, or what they are. Of course, we have the formulae for calcium fluoride and strontium fluoride, and I believe it will be possible one of these days, with a proper following up of the subject, to work out apparatus by which we can obtain vapor densities at very high temperatures. I will not put a limit to the temperatures; as in fact, the flame arc, under the high pressure of 22 atmospheres, has given the temperature of the sun, 6,000° C. (See O. Lummer's recent book on this subject, on very high temperature flame arcs under pressure.)

I have not laid any stress upon the question of the amount of time taken to volatilize a given weight of material in determining these boiling points. I have laid stress on the fact that one material volatilizes more rapidly than the other material (in same cup, at same time), to such a marked extent that even if I had taken the molecular weight or the atomic weight, the difference would be in the order stated, and it would be only in the case of very close approximation of the boiling points of the two metals that this indication would be in error. I have not selected metals so close together that they would come within this range, as far as I know it. I think all the actual figures (of boiling points of fluorides) are based on a differential volatilization that is extremely marked. The very small beads of metal and fluoride were volatilized together at the same time, from the same cup,

[4] Trans. Am. Electrochemical Society (1907), 12, 141.

to secure nearly isothermal conditions. The data represented hundreds of weighings. Moissan did not use this method. Also this isothermal temperature is that of the boiling point of the lower boiling substance.

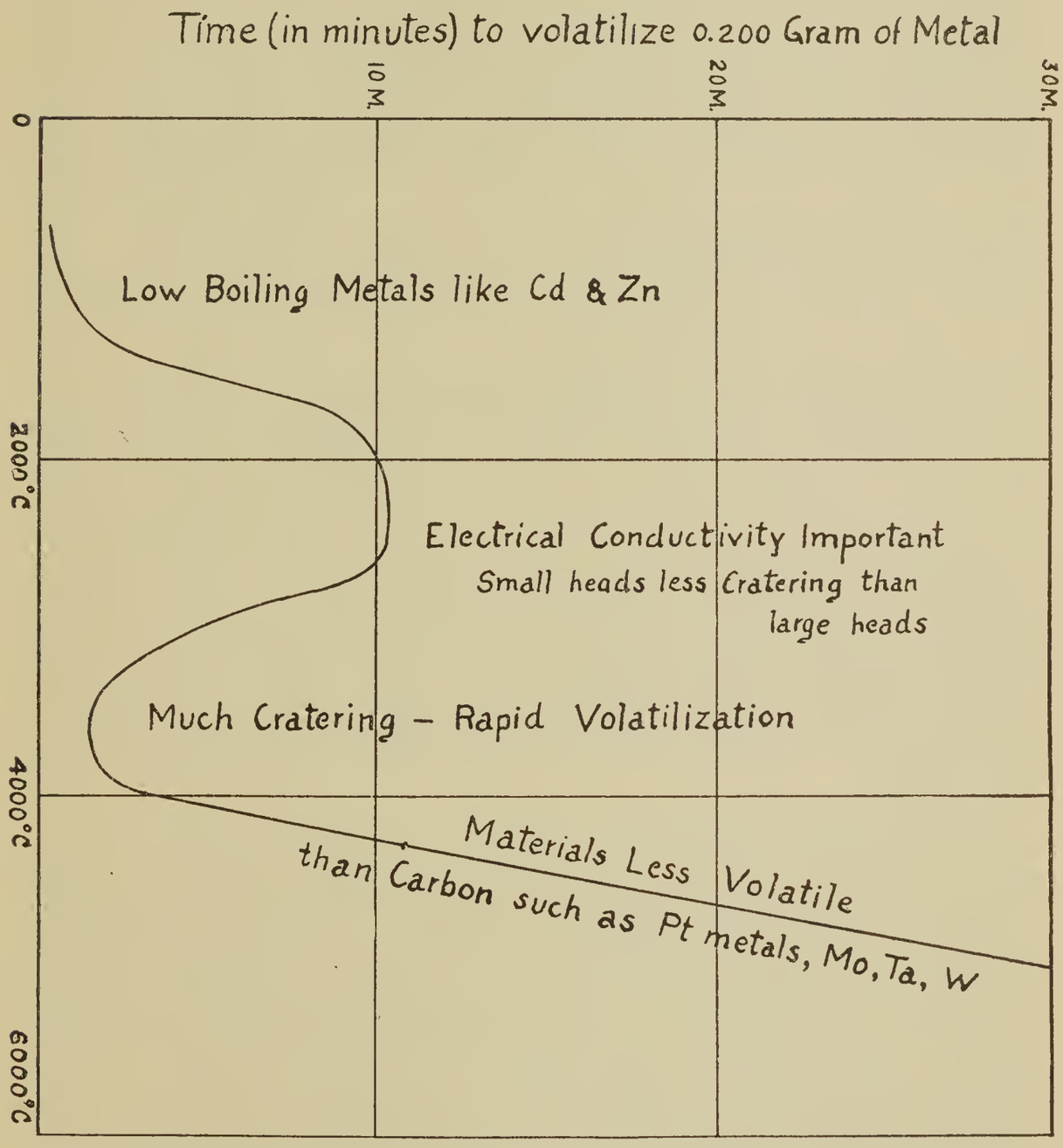
Speaking of Dr. Watts' paper, as I recall the paper it represents an excellent attempt to follow up Moissan's work, but was also unfortunate in the direction of particularly selecting the boiling point of tungsten as that of the temperature of the arc (3,700° C.). The boiling point of tungsten is undoubtedly considerably above 5,000° C., and Dr. Watts' choice of his upper reference point vitiates all his temperature figures.

When you volatilize a mixture and at the end have only one material left, it stands to reason that that material is of less volatility than those which have volatilized. If you should have, however, a mixture at the end which contained both materials, you are in a perplexity, and you will probably have to resort to other means to determine which is the least volatile, although I would say that if the residual mixture contains chiefly one of the constituents, it probably is the one that is the least volatile. Nickel is quite volatile as compared with iron. Pure iron has a boiling point around 3,000°, or about 3,300° C. when saturated with carbon. When you put nickel with the iron, however, it forms an alloy which has a decidedly higher boiling point than either of the metals alone, and in that case it would be pretty hard, boiling the two together, to conclude from that alone that the nickel was the more volatile, although it does go off to marked extent more than the iron does. This means that it is desirable to resort to other methods. (See paper, page 374, for reference to several factors controlled by boiling-point temperature.)

F. C. Frary[5]: I would take issue with Dr. Richards in regard to the importance of molecular weight in the matter, for the reason that what Mr. Mott is measuring is vapor tension of these materials at that temperature, which, from all we know, has no direct relation to molecular weight. Dr. Richards is speaking from the viewpoint of energy involved in volatilization, and what Mr. Mott was determining was the relative vapor tension at the temperature of the arc, which is another matter from the actual energy involved in the vaporization. Of course, the energy in-

[5] Research Chemist, Oldbury Electrochemical Co., Niagara Falls, N. Y.

volved would be dependent on the molecular mass, and for its determination you would want to use functions of the molecular weight. When you want to determine the vapor tension of any substance, it does not make much difference how much of the



Curve of Relation of Boiling Point of Metals to amount volatilized in Carbon Cup.

FIG. 3.

substance you use. What you are trying to find out here is the rate of vaporization, and that is a function of the material and speed of the hot gases. The relative rates of volatilization are measures of the relative vapor tensions of the substances in question. I think the results which Mr. Mott has given are exactly

the things we would want to know if we wanted to know anything in particular about these materials.

I was interested in the matter of the size and shape of the negative crater. The normal carbon arc, of course, has a very small hot spot on the negative pole, and we notice in two of the groups here, the thorium and radium groups, we get a spreading and diminution of the temperature, and instead of having a small hot spot on the negative electrode, we have a fairly large cool spot over the whole arc, and instead of being concentrated, the arc is spread out. The only explanation of that to my mind is the increased conductivity of the air next to the electrode. Mr. Mott is inclined to explain that on the ground of the formation of cyanide and the derivatives of cyanamid with some of these other elements. But it is hardly fair to assume the formation of such compounds at the temperature of the arc, as we know that these things are extremely unstable and unlikely to be formed. The more plausible explanation would, perhaps, be some sort of ionization effect of the air due to the radio-activity of the heaviest members of the group, the radium and thorium. It is known that barium, strontium and calcium salts all contain traces of such higher members, and naturally you should expect in the other groups traces of heavy elements, and these, owing to decomposition, give an ionizing effect on the air which would increase the conductivity.

W. R. Mott: Ordinarily, if you double the amount of material the time to volatilize only increases about two-thirds. The correction differs with different materials. If there is a marked crater on the metal itself the time to volatilize is greatly reduced. Many factors determine time of volatilization besides the vapor density. Averages of many metals are shown in Fig. 3, which indicates that with an open carbon cup there is a very rapid volatilization of metals boiling around 1,000° C., and again those around 3,500° C., where a direct crater on the metal is formed. Beyond this, very long times may be required for materials less volatile than carbon. The formation of the crater, and electrical and thermal conductivities, are factors even more important than vapor density, in some cases. Dr. Richards will agree with me, no doubt, that the time to volatilize a single material in a carbon cup is only roughly suggestive of its boiling point. The curve

is only roughly followed, as was to be expected from the great complexity of the factors involved. The upper part of the curve is better. It takes several hours to volatilize an amount of tungsten that was left from one-half a gram of barium tungstate; we had to saw off the little tip and put it in another cup several times in order to volatilize the tungsten completely. Nearly a foot length (30.5 cm.) of ½ inch carbon (1.27 cm.) was consumed, because of the low vapor pressure of tungsten at carbon crater temperatures.

D. L. MATHIAS[6]: Did you assume that volatilization started with the appearance in the arc of the color of the element under test?

W. R. MOTT: Yes; it comes immediately with every material except those few that give intermittent carbon and flaming arcs, and have boiling points much higher than carbon itself.

Going back to Dr. Frary's suggestion about radio-activity, it is good, although I am inclined to believe my theory is a better one, as I have investigated quite a number of elements and found it fitted closely to the facts. The complete decomposition of some of these carbo-nitrides calls for temperatures only slightly below that of an ordinary carbon arc.

The diffuse negative gives very low temperatures, as shown by very low luminosity. I believe the temperatures are low enough to permit of partial formation of the carbo-nitrides. The phenomenon does not start in the center of the negative crater, but some distance away a bright, luminescent ring comes and then gradually the very bright center of the negative crater disappears, and the entire area becomes dim, with a brighter shade often at the outer edges where more chemical reaction can take place. It takes one-half minute to form the dim negative crater with barium carbonate. However, addition to the barium carbonate of beryllium oxide causes the high temperature center spot to be retained, probably because beryllium oxide hinders the nitrogen reactions. This is a good test for beryllium oxide, because only a few materials cause this inhibition of reaction. If the phenomenon was radio-activity, the composition of the

[6] Metallurgist, Mackintosh-Hemphill & Co., Pittsburgh.

barium salt would not matter if actually deposited in or near the negative crater. With very high temperature arcs the radioactive possibilities need investigation, especially with uranium.

J. W. RICHARDS: I think it is true that at any given temperature that element which has the highest normal boiling point will have the least vapor pressure, and therefore if you are comparing two elements at a given temperature, the element which has the greater vapor tension at that temperature will have the lower normal boiling point. Further, the lower its normal boiling point, the smaller will be its molecular heat of vaporization, which is practically proportional to its normal boiling point, as defined by Trouton's law, which holds fairly well. I think the statement which I made, that the molecular weights should be compared, is correct, because the heat required to volatilize molecular weight is proportional to the normal boiling point and that temperature controls the relative vapor tensions at any lower temperature.

F. A. LIDBURY: What is the relation between vapor tensions and boiling point, as exactly understood?

J. W. RICHARDS: $\text{Log } p = -\frac{A}{T} + B$. That formula holds pretty closely for most of the elements and compounds whose vapor tensions we know, and the constant B is very nearly the same for different elements. It has a value of about 8.5 for most of the elements, so that practically it is not the pressures which are inversely proportional to the normal boiling point, but the logarithms of the pressures.

F. A. LIDBURY: Does the constant A vary with the substance in question?

J. W. RICHARDS: Yes, and is related closely to the heat required to volatilize molecular weight. The constant A divided by 4.57 gives the heat required to produce molecular weight of the vapor, which is, in the case of the metallic elements, the atomic weight.

W. R. MOTT: When we come to the arc and the volatilization of any given weight of material in the arc, next to the crater, it seems rather difficult at the present time to apply the molecular

formula or the atomic formula. It is complex in so many respects it seems that you should consider more factors than the time to volatilize. In fact, that is very necessary. For example, barium fluoride will soak into the carbon, as nearly all barium salts will; potassium fluoride will wet the carbon to a somewhat less extent, and sodium fluoride will wet the carbon to a still less extent. These materials, because they wet the carbon, will travel a greater distance away from the crater regions, and for that reason a flaming arc may exist for a longer period than would be calculated by weights (even if molecular proportions are taken). It is therefore desirable to use several methods and co-ordinate the results. Many different mixtures should be volatilized. The temperature can be obtained also by optical pyrometry with the beads, craters and black body coefficient. The extent and character of the crater on the material, or, if not cratering, then the crater distance, are especially valuable, as shown in my paper. The time to volatilize is also influenced by the electrode material. For example, graphite cups take two or three times as long to volatilize equal weights of the same fluoride.

J. W. RICHARDS: In the May, 1917 number of Metallurgical and Chemical Engineering Mr. John Johnson has used the same diagram which I have indicated, plotting the logarithms of the vapor tensions of the metals as inversely proportional to the temperatures. This is practically a plotting of the formula previously given. He does not bring out the fact which can be seen by a glance at the diagram that the lines converge towards a common point, and that common point is the constant B. The two which do not converge are the vapor tension lines of solids, and these converge at another point. The pressures over liquids converge to one point, and over solids to another.

W. R. MOTT (*Communicated*): Referring to the dim low-temperature diffuse negative craters given by using barium carbonate in the positive cup in air; I have repeated this experiment in an atmosphere free from nitrogen, by using carbon dioxide. The diffuse negative crater did not form except after admitting a small percentage of air to furnish the nitrogen. The nitrogen appears essential in this case. If the radio-activity mentioned by Dr. Frary were the essential factor, the nitrogen would not

have caused this difference. The increased conductivity is therefore caused by increased chemical activity due to nitrogen reactions, either forming or decomposing. The objection raised by Dr. Frary that at arc temperatures these nitrogen compounds would not form can be eliminated because the temperatures of these dim diffused negative craters are far lower than ordinary carbon arc temperatures. The efficient formation of barium cyanide and titanium carbo-nitride is best carried out by using electric furnace temperatures. Therefore, their point of complete decomposition (or highest temperatures of partial formation) must be extremely high.

I can now give additional data on arc colors of elements not previously given. Erbium in the carbon cup gives a bluish-green arc core and a broad green shell 0.15 in. (3.8 mm.). Erbium is more volatile than iron or yttrium. The intense red shell of yttrium came last.

The platinum metals are all less volatile than iron, and most of them of very inferior light-giving power. The arc colors were as follows:

Ruthenium, bright blue core, yellow shell 0.06 in. (1.5 mm.).
Rhodium, green core, dim, broad, yellow shell.
Palladium, bright green core, no shell.
Osmium, violet core, no shell.
Iridium, blue core, no shell.
Platinum, blue-green core, becoming more green at outer edges.

Finally, I agree with Dr. Fink that there is room for many papers in these new fields, and I agree with Mr. Little that the periodic law has an important place in many ways in the study of arc-light production. Many interesting phenomena were observed which could not be given in one paper.

A paper presented at the Thirty-first General Meeting of the American Electrochemical Society, in Detroit, May 5, 1917, President FitzGerald in the Chair.

THE "VOSMAER PHENOMENON"

By William C. Moore.

Abstract.

The light phenomenon occurring when two nickel electrodes are made the terminals of an induction coil was investigated as to the effects of using different electrodes, different pressures of air between the electrodes, and different gases between the electrodes. A theoretical explanation of the various effects is attempted.

A number of years ago, a patent was taken out by A. Vosmaer, of Haarlem, Holland,[1] for the production of light by means of a discharge between nickel wires serving as the secondary terminals of an induction coil. About the time of the expiration of this patent, a description of the phenomena involved was written by Vosmaer and published in the June, 1914, number of Metallurgical and Chemical Engineering.[2] In brief, when the wires used are of the correct size for the induction coil to which they are connected, and the distance between the ends of the wires is properly adjusted, the cathode wire fuses at the end, forming a small globule, which glows with high instrinsic brilliancy.

Through the kindness of Mr. David H. Browne, of the International Nickel Co., this laboratory received a supply of various sizes of nickel wire, with which Vosmaer's experiments were repeated and extended. For convenience, the results are designated as the "Vosmaer Phenomenon."

With a coil giving a normal spark three inches (7.5 cm.) in length, the results noted in Table I were obtained:

[1] Eng. patent 21,877 (1899).
[2] Vol. 12, p. 377.

TABLE I.

Kind and Size of Wire (Diameter in m.m.)		Anode Phenomenon	Cathode Phenomenon
+	-		
Ni 0.8	Ni 0.6	—	End melted formed ball; glowed intensely.
Ni 0.6	Ni 0.8	—	No glow—(too large?)
Ni 0.4	Ni 0.4	—	Oxidized, formed ball, glowed. Reversing current caused other electrode to glow.
Ni 0.4	Pt —	—	Pt. melted; ball formed; glow less intense than with Ni.
Ni 0.4	Small Fe	—	Ball formed, larger than with Ni. Glow less intense than with Ni.
Ni 0.4	C from lead pencil	Intensely hot spot on anode	C glows.
C	Ni 0.4	Intensely hot spot on anode	"Vosmaer" phenomenon.

On increasing the distance between the electrodes the light from the cathode became less brilliant, and finally went over into a nickel spark.

A 0.4 m.m. cathode and a 0.6 m.m. anode of nickel wire were now set up in a long glass tube closed at the end with rubber stoppers, the apparatus being so arranged that the air could be exhausted and other gases admitted. On exhausting the air till the pressure within the tube was 10 m.m. of mercury, no sign of the Vosmaer phenomenon was noted.

Instead, there was a violet glow over the entire length of both wires. On admitting air, the Vosmaer light appeared; the nickel cathode fused, formed a ball and apparently oxidized, and then began to glow. Again, an intensely hot spot was noted on the anode. On exhausting the tube while the coil was running, the Vosmaer light grew less brilliant and completely disappeared at 50 m.m. pressure.

Before this, however, a violet glow began at the ends of the wires and gradually extended back along the wires.

Readmission of air brought about a reappearance of the Vos-

maer phenomenon; increasing the pressure above normal, however, seemed to have no effect.

A series of experiments was now tried with different gases in the tube, using a 0.4 m.m. nickel wire cathode against a 0.6 m.m. nickel wire anode.

When natural gas was used in the tube, the discharge decomposed the gas; at first, the spark was very luminous. The carbon deposit collected first on the cathode; later on the anode; finally, a carbon bridge was formed which short-circuited the spark gap. This carbon was finely divided; with a long gap, carbon was deposited on the walls of the tube; the spark then jumped to the tube wall. There was no indication of the Vosmaer phenomenon.

With hydrogen chloride in the tube, the cathode was rapidly attacked and was soon destroyed, with the resultant formation of nickel chloride, in a very finely divided condition. There was some indication of the Vosmaer phenomenon.

Nitrogen, prepared from ammonium chloride and sodium nitrite and dried by passing through sulphuric acid, was passed into the tube. On starting the induction coil, the Vosmaer light developed as usual at the cathode; the cathode, however, was rapidly attacked. The spark proper was greenish. The anode showed the Vosmaer phenomenon at first, but this was prevented by speeding up the interrupter. The nickel at the cathode had the appearance of boiling.

On analyzing the above results, it seems that the following phenomena take place, in the order named, when the wires are of proper size and the gap is of the proper length:

1. On turning on the current the cathode becomes intensely hot at its extreme end, and soon melts.

2. The surface tension of the molten nickel is sufficiently great to draw the molten material up into a ball.

3. While (1) and (2) are taking place the outer portion of the fused mass becomes oxidized. This oxide adheres very firmly to the nickel; as it apparently has a higher melting point than nickel (1450° C.),[3] the nickel is protected from further

[3] Bureau of Standards, Circular No. 7 (1910).

attack and so is not used up. An equilibrium temperature is therefore soon reached; the facts that the ball when the energy is liberated is so much larger than the wire, and that the heat conductivity of nickel decreases very rapidly with the temperature[4] cause this equilibrium temperature to attain a high value. The high emissivity of the nickel oxide layer[5] explains the high intrinsic brilliancy of the little ball.

On the other hand, if the nickel compound formed, does not adhere to the nickel, the nickel is attacked, as occurred when the experiment was run in hydrogen chloride; if a low melting compound is formed, as when the experiment was run in nitrogen, the same thing occurs.

On the electrical side, the conditions for the proper development of the Vosmaer light are not less interesting than on the chemical. In the article above referred to, Vosmaer calls attention to the fact that the discharge we are discussing could be called a high-tension arc discharge. The recent paper of Prof. W. G. Cady[6] on "Unstable States in Arc and Glow" contains a discussion of the transition from the glow to the arc discharge, which would seem to apply here. The "Vosmaer phenomenon" is apparently a transition from the glow to the arc; the energy liberated at the cathode raises its temperature so that thermal ionization sets in. The ions so liberated ionize the air by impact; the positive particles so produced bombard the cathode, raising its temperature finally to what I have designated above as the "equilibrium temperature." In line with this explanation, the disappearance of the Vosmaer light when the pressure is reduced is easily understood.

As the pressure is lessened, the mean free path of the ions becomes greater; so much ionization is therefore not produced in the immediate vicinity of the cathode; as many positive particles cannot reach the cathode as formerly and no light is produced.

The induction coil used required about 6 amperes at 6 volts. While no candlepower measurements were made, the total light emitted from the glowing cathode was less than that given by an ordinary 3-volt flashlight. It is thus seen that this glowing

[4] Angell, Phys. Rev., **33**, 421 (1911).
[5] Burgess & Foote; J. Wash. Acad., **4**, 279-80 (1914).
[6] Met. Chem. Eng., **13**, 866; (1915); Trans. Am. El. Chem. Soc., **29** (1916).

cathode is out of the question as an efficient light source, and is of value chiefly as involving a number of interesting physical, chemical and electrical facts.

The writer's thanks are due several members of the Research Staff for their interest in these experiments.

Research Laboratory,
National Carbon Company,
Cleveland, Ohio.
July 15, 1916.

DISCUSSION.

W. R. MOTT[1]: I would emphasize the importance that should be attached to nickel as a high-temperature material. It resists oxidation except for a surface film which protects it from further attack. In my experiments on the carbon arc I found that nickel in the positive crater is almost the only element, except platinum metals (and some alloys), which remains shiny bright on cooling in air from arc temperatures. Also, nickel is almost the only metal, outside of the platinum group, which can plate out on the negative electrode (of a carbon arc) and give a bright metal effect usually in the form of lace-like beads.

C. G. FINK[2]: The interesting feature of this paper, I think, is that it suggests a very simple method of testing alloys suitable for high-temperature resistances; that is, alloys of the Nichrome type. Dr. Moore attributes the fact that the nickel electrode is not consumed to the non-volatility of the nickel oxide. That alone would not account for the stability of the electrode. There are other factors that enter. First of all, the oxide of nickel has a lower vapor tension than the metal underneath. Second, the oxide has a very high surface tension. Some oxide films are discontinuous and tend to flake off; other metal oxides tend to form globules rather than a continuous film; if the nickel oxide were

[1] Research Laboratory, National Carbon Co., Cleveland.
[2] Research Chemist, Edison Lamp Works, Harrison, N. J.

of either type the electrode would be rapidly consumed. Third, the nickel oxide formed is not readily soluble in the metal. In the case of copper oxide, you could not get that same phenomenon as nicely as you could with nickel, because copper oxide tends to dissolve in the metal itself. Accordingly, the best oxide for the purpose must wet the metal, it must have a higher boiling point or volatilization point than the metal, and it must have a low solubility in the metal. Therefore, if we are looking for an alloy which will withstand high temperatures, 1,300 or 1,400° C. or above, for heating devices, etc., it is not necessary to take a new alloy and draw it into wire to test it; all we need to do is to fasten a little globule of it to the electrode and try it out by Moore's method.

J. W. RICHARDS[3]: I wish some one who has the equipment would try out the various metals in about the same way that Mr. Mott has tried out these compounds, and give us the phenomena complete for all the elements. From this we could draw much more general conclusions.

W. C. MOORE: Dr. Fink's suggestion to use the Vosmaer phenomenon as a means of testing metals and alloys for withstanding high temperatures is very interesting and should merit further attention.

[3] Professor of Metallurgy, Lehigh University.

A paper read before the Joint Meeting of the New York Sections of the American Electrochemical Society and the American Institute of Mining Engineers, January 26, 1917, and called up for Discussion at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 3, 1917, President FitzGerald in the Chair.

THE HISTORY AND LEGAL PHASES OF THE SMOKE PROBLEM

By Ligon Johnson.

[*Abstract.*]

The history of injury by smelter smoke and fume is traced from the time of the Romans to the present, and the various legal enactments adopted by different countries in recent times are discussed. Smelter smoke litigation in various States, the appointment of smoke commissions, and the work of special research laboratories to study the question in all its various aspects, are discussed. The futility of suppressing only the visible smoke, and not suppressing the invisible deleterious gases, is pointed out.

Only the acute phase of the smelter fume problem is new. The problem itself is older than the Christian era.

While both lead and copper were mined and crudely smelted some three thousand years ago it was not until the Roman occupation of the Iberian Peninsula and the British Isles, which occurred but shortly before the beginning of the Christian era, that there was any evidence of smelting operations on a scale sufficiently large to permit a fume problem.

Around Huelva, Spain, are found more than 30 million tons of slag from lead smelting conducted there by the Romans. Pliny tells us that more than 20,000 slaves were employed in the Iberian mines. Extensive mining and smelting by the Romans in England and Wales were coincident with the Iberian proceedings.

These metallurgical operations were upon a sufficiently large scale to produce marked results both upon the surrounding country and the smelter workers, but, as these operations were those of a conqueror upon conquered soil, conducted by slaves, imperial Rome failed to recognize that such a thing as a smoke

problem did or could arise, and whatever fume question there may have been at that time remained a question only to those who had no chance to answer any phase of it.

The smelting operations of the Romans extended over about four hundred years, and little is recorded of lead and copper smelting from that time until the sixteenth century. From the revival, beginning at this period, up to the present century the growth of smelting has been comparatively gradual. In Great Britain smelting was conducted almost wholly in localities where metallurgical operations were of paramount importance, and the communities which grew up in smelter localities were due to and dependent upon the mines and smelters. This fact had much to do with the comparative freedom of British smelting from burdensome fume litigation and legislation. To a lesser degree these conditions applied to the German operations which, when coupled with the further fact that most of the early German operations were to a greater or less degree fiscal workings of Prussia, Saxony and Brunswick-Hanover, accounts for the early immunity of German smelters. Topographically and with relation to fertile farm lands, the locations of the British smelters were superior to the German, and ultimately a strong legislative barrier was erected around German operations, particularly in the case of new smelters and under new locations of old plants.

Nowadays, German smelting is, or at least prior to war conditions was, under supervision of special officials in the nature of mining police and courts. Before construction of a smelter could be begun, application for a permit had to be made, and this application accompanied by general data as to location, character, capacity, height of stack, character of ore to be treated and the like—where a permit was once granted, it was not revocable, but notwithstanding the permit, if damage was done the smelter could be required to change its methods and to install such appliances as would, so far as possible, prevent injury. Where a permit was refused, no smelter could be built. The refusal of a permit by the Berg-Polizei, or mining police, was not final, but an appeal could be had to the Berg-Gericht, or Mines Court, and finally to the Ober-Berg-Gericht, or Mines Court of Appeals, which was the tribunal of last resort. Incidentally the Berg-Polizei had inquisitorial or supervisory powers, not only as to damage to vege-

tation but also as to the safety of the works and the life and health of the employees.

It is supposed by many that the British Alkali act was aimed at the smelting industry. This is far from correct. The original acts were directed chiefly at the manufacture of soda, acids and ammonia. In 1861 the House of Lords provided for an inquiry "into the injuries resulting from noxious vapors evolved from certain manufacturing processes, and into the state of the law relating thereto." While the investigation covered smelting as well as the other enterprises, the resulting act (the Alkali Act of 1863) covered only so-called alkali works and provided for the elimination of not less than 95 percent of the hydrochloric acid produced in alkali processes. By an amendment of 1874 it was enacted that not more than one-fifth of a grain of acid should be contained in each cubic foot of gas (0.45 g. per cub. meter) escaping from the works.

The original act was made more comprehensive by amendments and revisions of 1874, 1881 and 1892, but other than operations under the wet copper process and certain zinc processes, it was not until 1906 that smelting generally was included; and, even then, no actual regulation was provided, as the act so far as smelting was concerned merely declared that the inspectors under the act "may inquire whether in any works in which sulphide ores are calcined or smelted, means can be adopted at a reasonable expense from preventing the discharge from the furnaces or chimneys of such works into the atmosphere of any noxious or offensive gas evolved in such works, or for rendering such gas when discharged harmless or inoffensive" (Act 1905, Sec. 8 (1)).

No limitation was placed on smelting operations beyond inquiring as to the installation of such remedial methods or appliances as might be installed at a reasonable expense. There was no prohibition as to tonnage or fume strength, and the first report of the inspectors touching on smelting was in the forty-fourth annual report of the department for the year 1907, forty-five years after the passage of the original act, and this embodies no smelter regulations.

Fume controversies and the attendant litigation and legislation are of comparatively recent origin in the United States. Probably the first thing in the way of legislation in this connection was

the ordinance of Oakland, California, enacted in 1872, prohibiting the erection or maintenance of any smelter within the corporate limits of that city. Subsequent California legislation was that of Contra Costa County, limiting fume strength, and by the State providing for a smelter commission to investigate the effect of fumes liberated in smelter operations. Efforts were also made to prohibit by legislative enactment the exit of stack gases containing more than two-tenths of one percent sulphurous acid gas content. This proposed legislation, however, was defeated. There has been little legislation, either by the States or municipalities of the United States. Not until heap roasting of ores rich in sulphur was practiced on an extensive scale was there any litigation of consequence in this country, and to the condition resulting from heap roasting may be charged no small amount of the prejudice by the farmers against smelters and belief by them of the complete destruction of vegetation, animals and soil vitality through smelter operations.

The basis of this prejudice and belief is easily apparent, even to this day, upon a visit to Butte, Shasta County, California; Ducktown, Tennessee, and places where heap roasting was extensively practiced.

During heap roasting, strong fumes, in dense volume, were liberated directly on the surface of the earth. These fumes were heavier than air and cold, being practically of atmospheric temperature. They did not float off in the atmosphere but hugged the ground, rolling along in front of the wind in constant volume until absorbed by the soil and vegetation. There was little diffusion and the radius of fume influence gradually widened with the destruction of each successive barrier of vegetation.

The topography of the country surrounding the roast heaps was, almost without exception, sharply declivitous, as the roasting operations were conducted in hilly and mountainous regions. The soils of the regions surrounding the smelter sites were coarse and grainy, requiring the binder of the roots of vegetation and humus to hold the soil particles together.

The destruction of plant life adjacent to heap-roasting operations resulted not only in the loss of vegetable life above the soil but the roots below, and with every rain the top soil was eroded until considerable areas were not only made wholly barren, but

the top soil washed away and only the decomposing rocks and mica were left. In consequence, there was no soil in which vegetation could find a foothold, even when the fumes were no longer present. It was from this erosion that the belief of the killing of the soil first arose.

From what they could already see, the people around the smelters believed the smelter smoke to be the veritable breath of the Upas tree which destroyed all within its reach, and that this deadly agency was daily reaching farther and farther from the smelter and in and upon the homes and farms surrounding the smelter sites. Litigation was then not only threatened but instituted. First the farmers sued the Tennessee and Ducktown companies and upon the failure of these suits the State of Georgia took up the cudgel. The farmers in Shasta County, Cal., brought suit against the plants at Kennett and Coram; the Benicia residents and adjacent farmers sued the Selby smelter; the United States, by reason of the ownership of a forest reserve, adjoining the Keswick plant, filed its bill against the Mountain Copper Company; not long after this, the Deer Lodge Valley farmers filed their suits against the Washoe Company at Anaconda, and Salt Lake Valley farmers began proceedings against the smelter operations in that valley. The epidemic of smelter litigation was under way.

With these suits developed the early so-called smoke experts. Most of them had been in the heap-roasting communities where the destruction of vegetation and soil erosion had followed the heap roasting. No definite knowledge of fume action was available, and the experts for both plaintiffs and defendants, in the absence of knowledge, began to form pet theories only to be met by pet theories of others directly at variance.

In the good old days of theory an expert could make a casual inspection; or examine a few cross sections of leaves under a microscope; or make a few comparative tests for the sulphur contents of healthy and unhealthy plants, and deliver an epic on what the fumes were and were not doing. The appearance of the country around the old roast heaps and early plants were too big a handicap for the smelters to overcome, and, with the notable exception of the Washoe litigation, in practically every case an injunction followed.

About the time of the institution of these suits the smelters began the abandonment of heap roasting and the development of present-day operations. In this development prior theories expounded by the then experts or testified in the smelter suits had considerable bearing. In one locality everyone was assured that the injury came wholly from the dust particles; in another from the dust particles as the nucleus for minute drops of acid; in another from sulphuric acid vapor, which could be seen as a white fume cloud, and practically everything was blamed more than the chief, if not sole offender, the SO_2. In many cases the courts followed these theories in their decrees.

The first development went to long settling flues, smoke houses and dust chambers, cooling and slowing down gases, and taking out so far as possible the solids and acid vapors. At the Tennessee plants acid making was attempted.

In most of the litigation, under readjustments to conform with decrees entered or modifications of these decrees, which modifications, as a rule, were secured under very substantial cash payments to the farmers, the smelters secured a new lease on life. Several, however, such as the Balaklala plant in California, and the Highland Boy at Salt Lake, were completely closed, and passed into history as smelters. Most of the new installations, methods and readjustments provided by the decrees were in conformity with the theories of the experts in that particular case.

It is interesting to note that not only were the findings of fact in the different cases widely at variance but the conclusions of law in many instances directly in conflict, even in cases in different circuits of the United States courts. For instance, in California and Montana the United States Court held that the court could consider the balancing of conveniences, that is that the court, in determining whether or not an injunction would be granted, could weigh the damage which would be done under closing a smelter against the benefits the farmers would receive under an injunction. In the federal court in Utah a directly contrary holding was made. In neither law nor facts did the courts coincide.

Some little time was required to make the plant changes to conform with the theories of the experts adopted by the court, and still further time was required to demonstrate the effectiveness

of the changes. Most of the theories failed to pan out, and gradually a new crop of complaints, and claims that the recent installation did not prevent the damage, began to grow. Some claimants were insistent. Plant managers, remembering the results of old litigation, sought to temporize instead of ascertaining the real facts and meeting them squarely. Some tried to buy peace.

Let me say just here that nothing in the Selby report is truer than the statement that (p. 14) "The policy that 'buys off' trouble, as the most expedient commercial method for abating it, has been responsible for much of the smelter litigation of this country and the intense ill feeling that unfortunately exists toward smelters in many smelter communities." It did not take long under this practice for the price of peace to rise to prohibitive figures, and a new epidemic of litigation was threatened.

Going back a little beyond this second period of threatened litigation and before the storm clouds of it were yet clearly over the horizon, I think that I may say that the smoke problem was then considered by most plant managers as the least of their troubles. Little or no thought or study was given the question, and when it was mentioned it was waved aside. The worst most of them feared was having to judiciously distribute a little peace money.

A number of the smelters, such as the Washoe, Mammoth, Bully Hill, the old Mountain Copper, the proposed Engles smelter and others were either in or adjacent to national forest reserves, and numerous reports of damage, or threatened damage, began to come into the chief of the Forest service and the Land office, which reports were in turn referred to the Department of Justice. I was at that time special assistant to the attorney general, and these reports were finally referred to me with instructions to prepare and file bills for injunction unless some satisfactory solution could be reached.

While it was probably unknown to the smelters generally at that time, it was never the intention of the Government to close any plant. What it sought was the immediate and serious consideration of the fume problem, and active effort to correct harmful conditions where such existed. Only one suit was filed, and that was against the Anaconda plant. In each of the other cases stipulations were entered providing for research work and the

installation of the highest types of methods and appliances known to smelting science, or else the abatement of the operations producing fumes in harmful quantities until such appliances had been installed and proven elsewhere, upon which they were to be installed at the smelter entering into the stipulation. In the Anaconda case the first scientific commission was agreed upon. We proposed that the smelter operate under the best type of methods and appliances known to science and commercially feasible at the plant, and that John Hays Hammond, Dr. Ricketts and Dr. Holmes, chief of the Bureau of Mines, be designated as a commission to investigate and prescribe what changes or installations should be made under the agreement.

It was not long after this that the threat of further litigation by the farmers became ominous, and, as I had completed my work with the Department of Justice so far as smelting matters were concerned, I resigned to become what might be termed smoke or field counsel for the American Smelting and Refining Company.

The first urgent smoke matter in this connection was the Selby litigation, between Benicia residents and the Selby plant, which had been pending a dozen or more years. A flat injunction against the operation of the Selby plant had been granted, which injunction had been fought through the courts and finally approved by the Supreme Court. The case had been through the court of last resort and the injunction was to become effective in a month or six weeks' time.

On examining the record I found this suit to be somewhat different from the average smelter suit. Very little claim of injury to vegetation was made. More stress was placed on injury to animals, but the chief ground of complaint was excessive discomfort and alleged nausea and illness produced by odors which the witnesses uniformly declared "to smell like rotten eggs," or the sulphur spring of an adjoining county, which spring gave off quantities of sulphureted hydrogen.

An examination of the Selby plant disclosed that, regardless of what lead loss there might have been at other times, under changes made or under way no lead loss would occur, and therefore no possible source of injury to animals could exist from the plant's

operations and that there was no appreciable amount of sulphureted hydrogen given off by or generated in the smelter plant.

In the San Francisco region in the spring and summer months constant trade winds blow and these winds follow a direct line from the Selby smelter to Benicia, where most of the complaining witnesses lived. Beyond the Selby plant, but also directly in line of the trade winds over the Selby plant, was a large oil refinery and asphalt works. The odors complained of by the witnesses all came in the early morning hours, and investigation disclosed that at the times involved in the testimony, the oil and asphalt stills were not capped and were poured at three or four o'clock in the morning. Here, then, was a source of odors, which odors traveled on the same winds that carried the Selby smoke. The smelter was guilty of none of the things upon which the injunction was based. Capping the oil and asphalt stills practically disposed of the unpleasant smells.

We notified the county attorney and commissioners of Solano County of these facts, and stated that we proposed to decline to observe the injunction prohibiting the operation of the plant. This would mean additional long-drawn-out and expensive litigation. To obviate such a situation I proposed that the whole matter be referred to a commission of scientists of the highest type, the members to be agreed upon jointly, and the finding to be entered in the Selby case as the findings and decree in that case. Every access to the plant and fullest facility for examination was to be given the commission. After many conferences an agreement along these lines was arrived at and the Selby Commission came into being. The members of the commission were Dr. J. A. Holmes, Director of the Bureau of Mines; Dr. E. C. Franklin, then Director of the Chemical Laboratories of the U. S. Public Health Service at Washington, and Ralph A. Gould, a chemical engineer of San Francisco. With the Selby Commission came the first scientific research in smelter fumes along the lines of normal field conditions.

The examination of the Selby Commission extended over a period of about a year and a half, and in the end clearly demonstrated that the smelter was doing none of the things found against it in the original decree; and the injunction was vacated.

Shortly after the time the Selby Commission began on its work

the murmuring of discontented farmers became much louder. Crops had failed in many localities, and wherever this crop shortage was in a smelter locality the smelter was blamed. This was particularly true where prior payments had been made to farmers. Peace was quoted at war prices.

As I before stated, this was very shortly after the Selby Commission began its work. Other than the research just beginning under the Selby Commission, there has not been in the United States or elsewhere any experiments or research work with smelter fumes or SO_2 under natural field conditions. It is true that Haselhoff and Lindau, Von Schroeder and Reuss, Schroeter E., Wieler and Hartleb, Hartig R., Wislencenus, Freitag, Sorauer, Ramaun, Gerlach, Schmitz-Eumond, Sabachnikoff, Raubner, and Stockhardt in Europe, and Haywood and Pierce and to a limited extent Ebaugh and Talmage, in the United States, had carried on some experiments, but in none of these were normal field conditions approximated. Some fumigations were carried on with leaves or twigs or small parts of plants in bell jars. Others were in hermetically sealed cabinets or "smoke houses," so constructed that only abnormal conditions could result. The plants used were grown in pots or flats and were grown and kept under conditions that were not normal. The fumes introduced were from burning sulphur or sulphur and alcohol or else concentrated SO_2 let in from a tank or gas burette. The concentrations were unknown, absorption was not considered, nor were chemical analyses of the air made. Environmental factors of temperature, humidity, light values, barometric pressure and time element of exposure were not considered. The plants used in the experiments were not grown to maturity, nor were their food or crop values ascertained. As a matter of fact, at the time these experiments were conducted, no quick and accurate method of air determination was even known to the experimenters. Even had these investigations been conducted with normal plants, under natural field conditions, the lack of knowledge or records of actual fume strengths reaching the plants and of the environmental factors involved, would have rendered the experiments practically valueless.

Some investigators of smelter regions placed much reliance on the sulphur content of plants collected in smelter neighborhoods,

notwithstanding the fact that investigations in the Department of Agriculture have shown that the sulphur content of the same plant may vary as much as three thousand percent at different times during the season, and at the same period the content of the same species of plant will vary markedly, particularly under different percentages of soluble sulphur in the soils, which frequently occurs at short distances.

In other words, from farmers and experts the smelters were coming in for full blame for all crop failures, and the managements actually did not know whether or not they were doing the damage. From my past experience, I knew that there were numerous plant injuries attributed to smelter smoke which even the most competent expert could not differentiate by mere observations or even microscopic study. Numberless diseases and injuries which were not caused by smelter smoke were pointed out as evidence of smoke damage.

No plant manager knew how much, if any, of the damages attributed to the smelter was caused by it, and if there was damage, that operation of the smelter or element of waste had produced the damage. And, too, with the payment of damages communities of smoke farmers grew up. Their idea of farming was to let their places grow up on weeds and collect from the smelter the value of the maximum crops ever produced. Many smelters had paid damages for conditions which, it later developed, were not remotely attributable to smelter operations; but the farmers once having been paid insisted on continued payments. The price of peace was rising above the possible profits of smelter operations.

The time for theorizing had passed. It was necessary that the smelter managements know just what damage, if any, was being done, and if there was damage, how it was done and what was necessary to prevent such damage. Under my urgent recommendation, the first research department to ascertain all this was installed, and it, in conjunction with the Selby Commission, blazed the way for "smoke engineering."

This research work involved chemistry, plant pathology, plant physiology, entomology, agronomy, dairy husbandry and veterinary toxicology and meteorology.

You may wonder why all this was necessary just to find out

whether or not the smelter was doing any of the things claimed, and why one or two experts familiar with the appearance of vegetation in smelter regions would not have sufficed.

We had to know first what smelter fume or parts of fume would do damage, how the injury could be caused, what conditions were or could be confused with smoke injury, and finally, where damage was or could be done, what steps were necessary to obviate it.

This meant first extensive research work under normal field conditions to ascertain the effect of smelter eliminations upon vegetation and animal life. The time at hand is too short to go into a minute description of this research work. It will probably suffice to say that we found that dust and acid vapors were practically negligible quantities in the fume problem so far as vegetation was concerned. Where damage was done, this could be traced almost, if not wholly, to sulphur dioxid. The average vegetation can stand fifty times the strength of acid vapor that it can resist where the sulphur is administered in the form of SO_2. In the average smelter fume the acid vapor is but a small fraction of the sulphur content, this latter being chiefly confined to sulphur dioxid.

It then became necessary to ascertain the relative resistance of the various plants to sulphur dioxid, and the conditions under which inquiry occurred when the SO_2 was present in sufficient quantities to do damage.

To develop this fact it became necessary to know exactly how smelter fume acted upon plant life, how it obtained ingress to the plant structure and its effect after its absorption in the plant.

It may not be amiss just here to describe in a few words how this ingress comes about and the results which follow. In the beginning we found that only during the period the plant was in leaf could injury occur. Subjecting a plant to SO_2 or other fume while not in leaf produced no result. In most instances, and practically without exception in alkaline soils, we found that treating the soil in which the plants grew with sulphur or sulphuric acid, that is, dusting or spreading crude sulphur upon the soil or spraying the soil with acid, resulted in increased crop yield. Sulphur administered in this way was a benefit and not an injury. This conclusion was verified by independent experiments con-

ducted at the University of California in Berkeley, at an experiment station in Oregon, and at the experimental farm of the Anaconda Copper Company.

The question then narrowed down to the effect of smelter fume through leaves and on leaf structure, and to present this clearly it is necessary to describe the ordinary leaf and its functions.

All leaves under normal field conditions, in climates such as we have to deal with here, have an epidermis covering both under and upper leaf structure. This epidermis is impervious to moisture, and for all practical purposes, except where stomata or breathing pores occur, is also impervious to gases. These breathing pores are so small that considerable magnification under a microscope is necessary to see them at all. The stomatal openings are entirely too small to admit the minutest suspended water globules or particles of mist or vapor. The stomata at the leaf surface are faced with two guard cells, that are also covered by practically impervious epidermis, which guards cells, under certain leaf functions open or close the stomatic chamber. With the guard cells closed, the leaf under ordinary conditions presents impervious surfaces to the elements. The inner content of the leaf or the mesophyl is composed of palisade cells, collecting cells and sponge parenchyma, in which, under the action of light, starch and sugar are formed and plant food manufactured and supplied the plant.

We next found that under conditions of absolute closure of the stomata, the plant was a number of times more resistant to SO_2 than when the stomata were open. Under all ordinary conditions the stomata forms the point of ingress of gas. It followed, therefore, that when an external condition brought about the closure of the stomata it brought about increased resistance, and we finally worked out four factors in chief in fume injury, where sulphur dioxid is present in strengths sufficient at any time to bleach plant life, these factors being light (the stomata are closed during the darkness), humidity, temperature, and constant wind direction. The bearing of the latter comes from the fact that injury, except from abnormally strong fumes, does not come from mere fume puffs but from steady application of SO_2 for several hours. The other three factors bear upon stomatal opening.

After we had learned the strength of SO_2 necessary to produce

markings upon plant life under field conditions, it became necessary to know whether or not SO_2 was present in such quantities in the field. It was also necessary to know accurately the wind constancy and direction, the limits of the smoke stream, temperature, humidity, and general weather data. Complete installation of standard weather instruments, under the supervision of the local U. S. Inspectors, was made; and portable laboratories, that is laboratories set up in small automobiles which could follow the smoke stream as well as make general tests, were secured. This was in addition to the fixed air stations maintained. Under the method of air analyses devised by J. R. Marston and later refined by Mr. A. E. Wells, chief chemist for the Selby commission, quick and accurate determination of air samples was possible, and, more important still, these samples could be taken in a few seconds' time and, in this way, the constancy or inconstancy of the SO_2 determined. For the smelter plants, we cross-sectioned the several flues at the base of the outlet stacks, and the stacks, to afford analysis of their contents, and installed self-recording thermometers at appropriate points in the flues and stacks for accurate and complete data as to gas temperatures.

With this knowledge the next step was to ascertain with scientific exactness the cause of crop failure or injury where the appearance of external conditions, and often even microscopic cross sections, were seemingly identical with the results of smoke injury, but where our other investigations had developed that smoke injury could not have occurred. There are many diseases, pathological conditions, and insect injuries which, both externally and under the microscope, present an appearance practically identical with that of smoke injury. With the completion of this investigation, a survey of the entire so-called fume zone followed.

It is interesting to note that in determining the injury of plants by disease we can establish our diagnosis with a scientific exactness not possible in the diagnosis of any disease of human beings or animals. We can establish our diagnosis beyond the possibility of doubt or question. This is done by what is known as the pure culture method. The unhealthy plant is pricked by a needle-pointed instrument which in turn is dipped in a special and pure plant jelly and a culture of the disease organism grown. The

disease organism is isolated with this culture and after the disease develops comparison of appearances are made; a second culture is made from the inoculated plant and a second inoculation of a healthy plant follows, and in this way the disease organism is isolated, the disease and appearance reproduced and the diagnosis established beyond a reasonable doubt. For insect causes, we find and collect the causative insect. As some insect colonies, although numbering thousands or even millions, are so small that the individuals are only observable under very high-powered microscopes, and others work wholly out of sight and beneath the soil, it requires a competent entomologist to handle this phase.

It will suffice to say here that we proceeded through the whole list of plant pathology, physiology, entomology, agronomy and dairy husbandry and veterinary toxicology with equal care and certainty. The time is too short to go into detailed explanation of the plan pursued under each.

One other agency in smoke determination has been established with relation to plant life, and that is the evidence of so-called guide plants. There are certain plants, such as barley, which are especially susceptible to fume injury, and will show bleaching long before the possibility of injury to other plants. Where the guide plants are unmarked, it is self evident that the trouble with adjoining hardier plants is not smelter smoke.

In the work I have mentioned, we not only secured information valuable to the smelters but we accomplished actual and beneficial conservation so far as the agricultural resources of the country were concerned.

Scientific farming is not yet widely practiced. Farming methods are often handed down from father to son. Year after year the same crops are planted, often on the same soil. This applies to farming generally, and not merely to smelter communities.

In many places not only do the soils become impregnated with disease-producing fungus and germs, but the result becomes so widespread that no healthy seed can be secured in the community. It often happens that disease conditions may largely be eradicated by proper treatment and planting of the seed and crop cultivation, but these facts, as well as that the seed is diseased, are unknown to the farmer.

I recall a case where enormous claims for loss of potato crops were filed against a smelter. Upon investigation we found both the potatoes and the soil of the region highly infected with two of the most disastrous of potato troubles, rhizactionia and fusarium. A subsequent search of the seed stores in the community failed to disclose a single healthy sample of seed. Naturally the potato crops were failures. The sad part of it was that there was no need of this loss. Healthy seed procured elsewhere and planted in soil where potatoes had not been grown for several years, would have given the old time record crops, and proper treatment of the local seed would have produced infinitely larger returns.

Most of the diseases and insect conditions of agricultural communities are largely preventable, and for those that are not, steps may be taken to greatly reduce the harmful effect. Much of the troubles can be directly pointed out to the farmer, and the means of eradicating or lessening these troubles shown him. This, of course, involves the demonstration that the unhealthy crop conditions are not attributable to the smelter.

The farmer who follows the suggestions for eradicating unhealthy conditions soon finds his crops exceeding those of his neighbors who have failed to observe the same precautions. In this way, gradually, it is true, the influence of the smelter's experts is felt, a friendlier feeling is engendered, agricultural conditions are improved and actual conservation accomplished.

This brings us down to one final theory which in some places is still firmly entrenched and threatens possible trouble. I refer to visual clearance, and the belief that anything seen coming from a smelter stack should be labeled with a skull and cross bones. Our investigations showed that the visible fume was little to be feared as an actual instrument of damage to vegetation. Under former operations where a good part of the lead content of the ore was blown up the stack and where heavy arsenic fumes were given off, this metallic loss had some connection with certain animal troubles but had little effect on vegetation. Where this character of loss was not involved, the visible fume was and is chiefly dangerous from the psychological point of view. By this I mean that most farmers (and many will be honest in their belief) will assert, so long as there are visible stack eliminations,

that every crop failure is due to the smelter fumes. Therefore, to meet this, it will be advantageous to obtain the greatest possible clearance up to the point—and I want to stress this especially—where the efforts to secure visible clearance renders the smelter operations more liable to do actual damage. Beyond this point it is better to try to educate the farmer and get rid of the belief. Just because a farmer sees dense volumes of soft coal smoke pouring from the stacks of manufacturing plants, business houses, engines and the like, he feels no uneasiness about his crop. There is little if any more danger to crops in the visible smelter smoke. And, too, even where the belief of damage is deep seated, mere belief can be met by facts, but actual damage cannot be dodged because the smelter management seeks to meet some psychological condition; for mere belief wont last long in the fact of actual damage.

Get clearance first for actual recoveries, and loss of toxic solids, and next, so far as possible, to meet any psychological conditions, but do not place visual clearance above the likelihood of actual damage.

Our investigation and the temperature curves we have worked out have shown us that where there is fume injury the answer to the problem is in hot gases, gas dilution, and high stacks. Anything that cools or slows down the gases, or results in their liberation at low altitudes invites, to say the least, the probability of actual damage. Promising a community complete visual clearance or encouraging the belief that visual clearance means impossibility of damage, is borrowing trouble for the future, for such a clearance, unless I am mistaken, means low gas temperatures.

These smoke problems are bringing to the front a new specialist, the smoke engineer. The far-sighted smelter management, under existing conditions, for all new constructions, and even alterations and additions to old plants, will find this new expert a necessity rather than a luxury. The best way to take care of trouble is, not to stop it after it is started, but to prevent its starting. Many of the smelters realize this and those that do, in the matter of the fume problem, welcome the coming of the smoke engineer and specialist.

DISCUSSION.

J. W. RICHARDS[1]: This subject is of considerable interest to electrochemists, because there has already been one suit against an electrochemical company for allowing deleterious fumes to be emitted into the air, and it is likely that there may be others. Mr. Ligon Johnson, who is eminently qualified to write upon the subject, brings out particularly the value of experimental research in sweeping away our traditions, many of them without any real basis and not settling the real questions at issue, and it required research of a high order in a good many directions, to settle the question. The paper is very effective in that sense; it shows the order of procedure for attacking a difficult question, and shows how thereby facts are brought into harmony where before there was nothing but discord.

[1] Professor of Metallurgy, Lehigh University.

A paper read before the Joint Meeting of the New York Sections of the American Electrochemical Society and the American Institute of Mining Engineers, January 26, 1917, and called up for Discussion at the Thirty-first General Meeting of the American Electrochemical Society, held in Detroit, May 3, 1917, President FitzGerald in the Chair.

SOME THEORETICAL ASPECTS OF ELECTRICAL FUME PRECIPITATION.

By W. W. Strong.

[*Abstract.*]

The development of electrical fume precipitation is briefly described. The theoretical aspects are discussed at length from the standpoint of the corona discharge about a centrally-placed electrode, showing the different regions about it in which exist positive space charges, ion formation, and negative space charges. Irregularities in the corona discharge caused by deposits on the central wire are discussed, causing brush discharge and inner and outer corona gas eddies. The mathematical formulas governing the operation of such a process are developed and their application explained. The time of deposition and path of the fume ions in the treater are discussed, and the precipitation constant for different size pipes and different temperatures determined. A bibliography of related scientific articles by the author is appended.

The subject of electrical precipitation illustrates very well the relation between the technical development of a process and the state of our knowledge of the process itself. The practical application of the electrical precipitation of fumes was first made by Lodge and Walker about 1883. At that time absolutely nothing was known of the mechanism of the conduction of electricity in gases. The technical development of the subject was sufficiently far advanced to have made the application of it successful if the proper kind of high-voltage generating apparatus would have then been available. Lodge and Walker, however, had to depend upon an electrostatic machine for their source of corona current and, of course, could never obtain sufficient current to precipitate fumes from any considerable volume of gas.

About 1895 Dr. Cottrell[1] took up the application of electrical precipitation to the removal of certain sulphuric acid mist and smelter fumes from gases. At this time the theoretical development of the conduction of electricity from gases had been very considerably advanced. Dr. Cottrell, however, obtained his success through the fact that the technical development of high voltage generating apparatus had made it possible for him to use enormously larger currents than Lodge and Walker had been able to do. Since Cottrell started the above work, the technical advances in electrical apparatus used for producing high-voltage currents has been very rapid, and it is owing to this condition that the art of electrical precipitation is now becoming so widely applied.

The theoretical advances of our knowledge of the state of a gas or fume inside of the electrical precipitation treater has in the meantime advanced but little, though it is true that the phenomena of ionization in gases has been tremendously advanced in the past fifteen years. These advances, however, pertain more to the conduction of electricity in gases at low temperature, to the ionization produced by radio-active substances and the discharges taking place in arcs and sparks. In the process of electrical precipitation the ionization of the gases invariably takes place at atmospheric pressure and in a region of space in which the electric field is very powerful. Unfortunately, very little has been done from the scientific point of view upon this phase of the conduction of electricity in gases. This subject will form a large part of this paper.

The theoretical aspects connected with the electrical precipitation problem can be roughly divided into two groups, those pertaining to the purely theoretical problems of the phenomena of the corona discharge in fumes and smoke and the subsidiary problems relating to the installation and operation of electrical precipitation apparatus. In the last group arise problems such as that of the generation of high-voltage uni-directional corona currents, the design of insulators that can support high voltages in gases containing fumes, mist and smoke, and subjected to considerable temperature fluctuations, the problem of the flow of gases through a treater containing a large number of pipes, the

[1] Cottrell, Problems in Smoke, Fume and Dust Abatement, Smithsonian Report, 1913.

problem relating to the effect of various frequencies of the voltage of precipitation, and others of a similar nature. A number of these problems have been considered in Mr. Bradley's paper, and for this reason and others this group of problems, especially as they are more or less subsidiary in the art of electrical precipitation, will not be treated here.

THE PURELY THEORETICAL ASPECTS OF THE PRECIPITATION.

The conduction of electricity in gases as regards their commercial application is of two types. In the one type the electrical current is partly or largely carried by electrons or ions that have come from the electrodes between which the gas is situated. As an example of this type of discharge, we might cite the electric arc. In this case the current is carried very largely by ions emitted by the electrodes and by the metallic vapor distilled from the electrodes, the gas itself not playing an important rôle in carrying the current. In the second type of electrical discharges in gases, the current is carried entirely or almost entirely by ions formed of the gas molecules. Examples of this type are those of the fixation of atmospheric nitrogen, the formation of ozone and the electrical precipitation of suspended matter from gases. In all these cases the effort is made to prevent the electrodes from playing any part in the conduction of the electricity except that of providing the electric field to which the gases are subjected. In the fixation of atmospheric nitrogen the electrodes are frequently cooled by water or by other means. In the formation of ozone and in electrical precipitation it is not found necessary to cool the electrodes.

In treating the phenomena of the electrical discharge in precipitation treaters, the simplest type of treater from the scientific point of view will be used, this consisting of a wire axially placed in a cylinder, the wire and cylinder being maintained at a high difference of electric potential. Under these conditions the gas about the wire is made luminous, this luminosity appearing as a halo or corona when the wire and pipe are viewed end on. The first application of apparatus in engineering work in which a discharge of this kind took place was that of high-voltage transmission lines. In these cases the discharge was always located about the immediate vicinity of the wire and was usually more

or less uniform when viewed end on. Electrical engineers termed this "the corona discharge." In the case of electrical precipitation, however, the discharge takes place a much greater distance from the wire, and often presents a brush-like appearance, resembling the electrical discharge from points. For this reason the electrical discharges in precipitation treaters has often been spoken of as a "corona," a "point" or a "brush" discharge. The inconvenience of the use of these terms is immediately apparent and it seems best to always refer to the discharge as the "corona discharge," even though the appearance of the luminosity is not uniform. The brush-like discharges in the corona may then be considered as constituting part of the corona discharge.

The electrical precipitation process from the theoretical point of view can be divided into (*a*) the formation of ions, (*b*) the charging of the fume particles by the ions, (*c*) the driving of the fume ions to the passive electrode, and (*d*) the collection of the fume at this electrode. If no ions were formed, if the ions could not be made to stick to the fume particles, or if the fume ions could not be driven to the collecting electrode by the electric field, electrical precipitation of fumes would be impossible. The ease of formation of ions depends upon the kind, temperature and pressure of the gas. Neglecting the effect of space charges, the formation of ions in a gas probably is not greatly affected by fumes and smoke, though it may be to some extent by the presence of vapors. The nature of the fume particles probably greatly affects the ease with which fume particles hold ions.

Some fume particles, composed of material such as zinc oxide, may cause a reflection of the ions that collide with them. Under these conditions a thin layer of some conducting substance over the surface may make it possible to charge the fumes. This does not mean that a vapor should be added to the fume and the temperature lowered below that of condensation, because films of impurities are known to adhere very tenaciously to solids. The persistency of impurities in adhering to surfaces of solids is shown by the filaments of electric lamps.

A word should be said as to the nature of ions. The smallest known ion is the electron, about 10^{-13} cm. in radius. Electrons may exist in the corona current in precipitation treaters, but most of the current is carried by what is called simple ions, *i. e.*,

charged molecules or groups of charged molecules that carry a charge. The radius of such an ion is 10^{-7} to 10^{-8} cm. Charged fume, dust or smoke particles become charged by electrons or simple ions colliding and sticking to them, thus forming fume ions. The size of fume ions ranges from the larger ones that are visible down to dimensions of about 10^{-5} cm. radius. The term "fume ion" is thus defined, and varies with the kind and condition of the fume, dust or smoke and the amount of electrical charge which it carries.

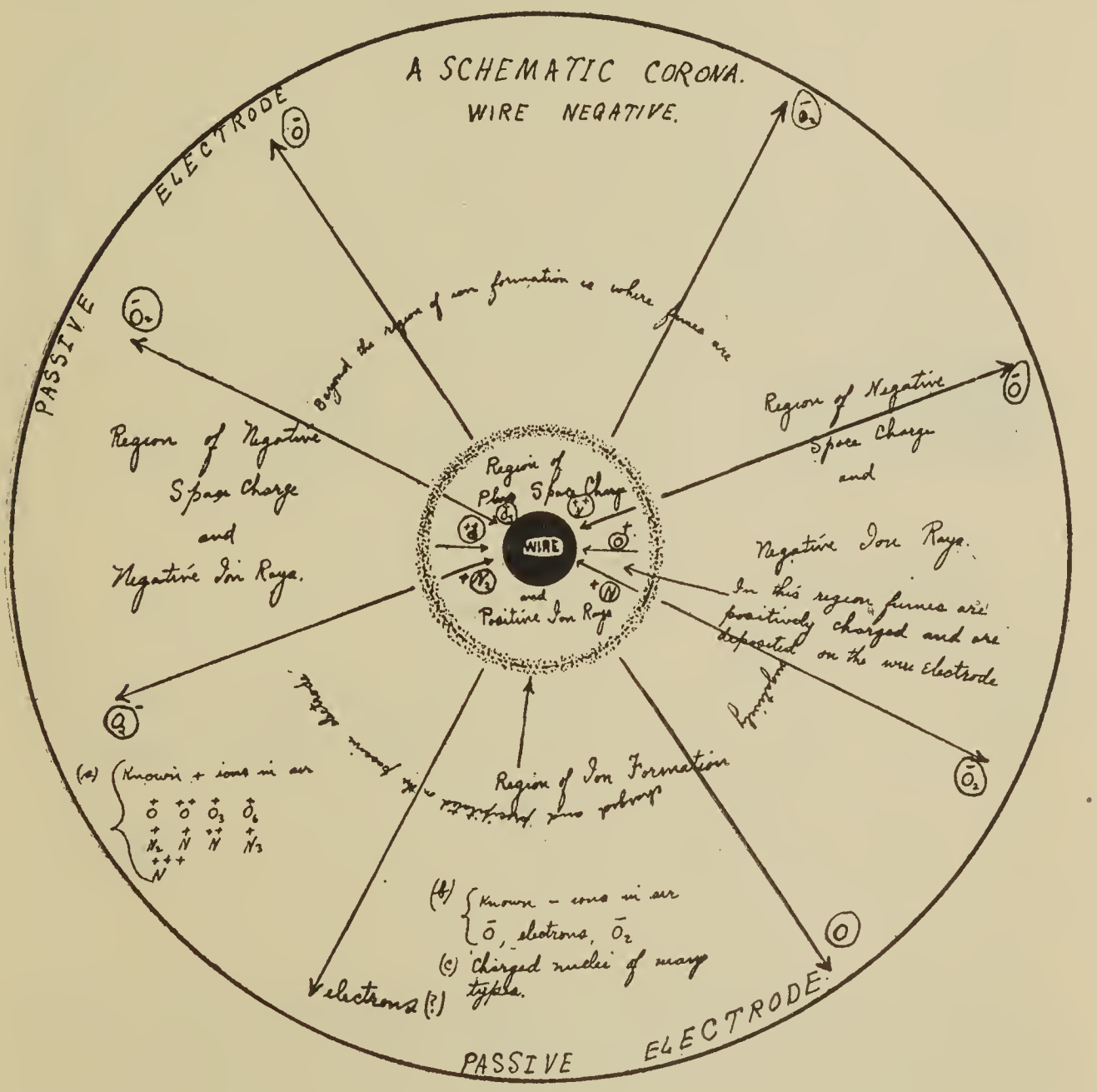

A SCHEMATIC CORONA.
WIRE NEGATIVE.
ELECTRODE
PASSIVE
Region of Negative Space Charge and Negative Ion Rays.
Region of Negative Space Charge and Negative Ion Rays.
In this region fumes are positively charged and are deposited on the wire electrode
WIRE
Region of Positive Space Charge and Positive Ion Rays
Region of Ion Formation
(a) Known + ions in air
(b) Known − ions in air
(c) Charged nuclei of many types.
electrons (?)
PASSIVE ELECTRODE

FIG. 1.

The Corona.

The nature of the space charges is shown in Fig. 1. In the region of the wire electrode is located the active electrode rays (consisting of positive ion rays if the wire is negative) and a

space charged by these rays (region of active electrode space charge); the region of ion formation where ions are formed by the collision of ions with gas molecules and hence a region where the electric field gradient is very great, and which is also the region of the passive electrode rays where the space charge has the same sign as that of the active electrode. These regions of the corona, *a*, *b* and *c*, are characterized by different precipitating properties.

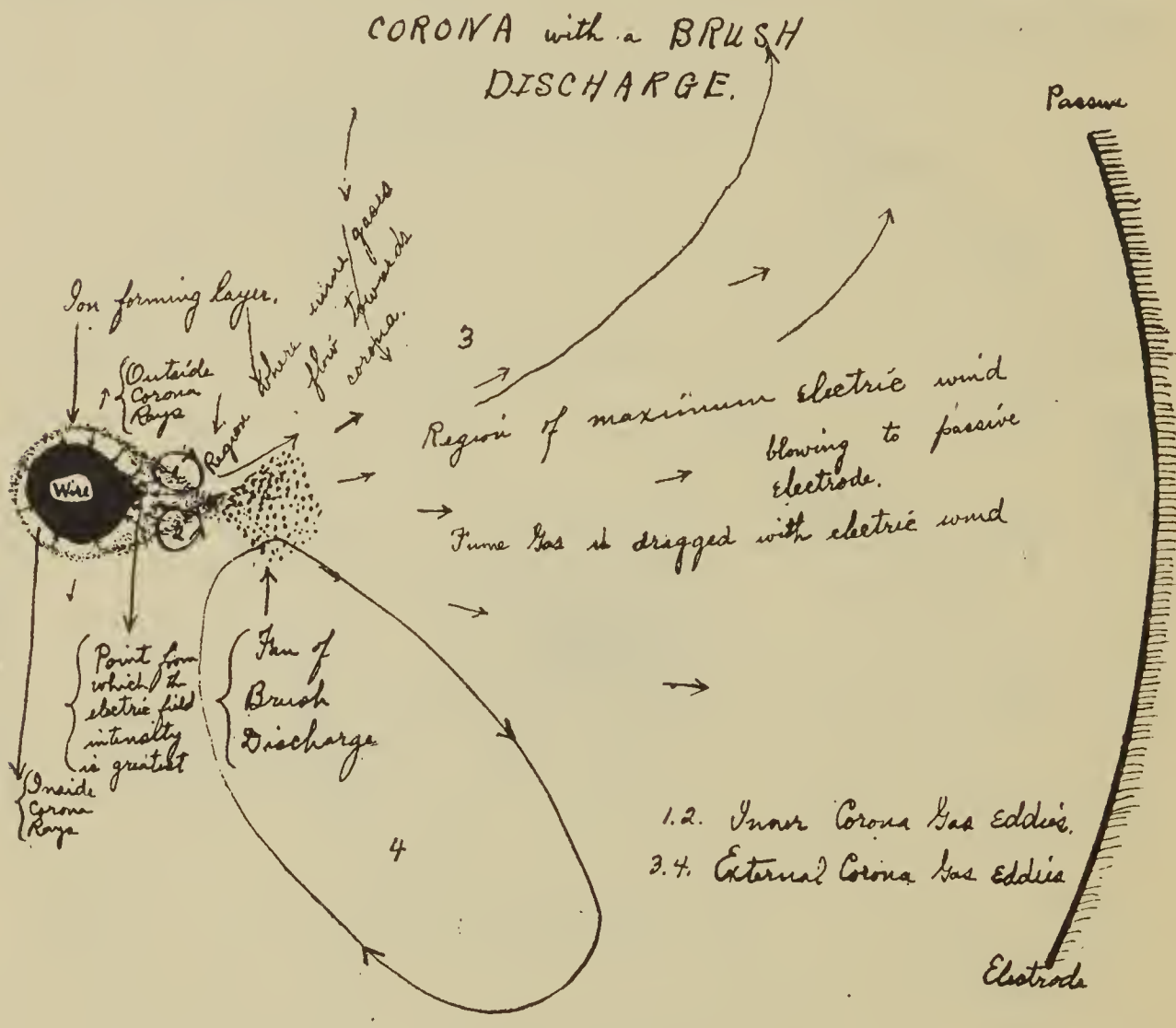


FIG. 2.

Fume or smoke particles that get into the region *a* are charged and attracted to the active electrode. Fume or smoke particles that get into *b* may be charged with either sign of charge, and may accordingly be driven to either electrode. Fume or smoke particles that get into the region *c* are charged so that they are precipitated upon the passive electrode. In the precipitation of fumes it is always best to prevent the fumes from entering the *a* and *b* regions, where they become precipitated upon the active

electrode and cause trouble by interfering with the corona discharge.

The quantity of space charge in a pipe depends upon the nature of the ions and the electric potential impressed on the electrodes. These problems will be more fully considered in a later communication. The effect of space charges is to decrease the quantity of ionization and hence choke down the corona current.

Fig. 2 illustrates how a corona may become unbalanced by the presence of deposits on the electrodes, by a non-uniformity of the fume gases in the treater, and also by the nature of the corona discharge itself. The unbalancing of a corona from its symmetrical discharge about a wire electrode results in the discharge being localized in certain parts of the treater. The pressure of the fume gases is greatest in the localized corona regions, and this sets up eddies in the gases as indicated. Fumes are therefore more likely to pass through that portion of the pipe where the corona is least intense. In a treater consisting of a number of pipes there is always a possibility of the corona becoming localized in a few or even one of the pipes. This localization of corona may take place without the formation of sparks or arcs.

Ionization in the Corona.

Fig. 3 shows how a corona current starts and the nature of an ionization current in a gas.

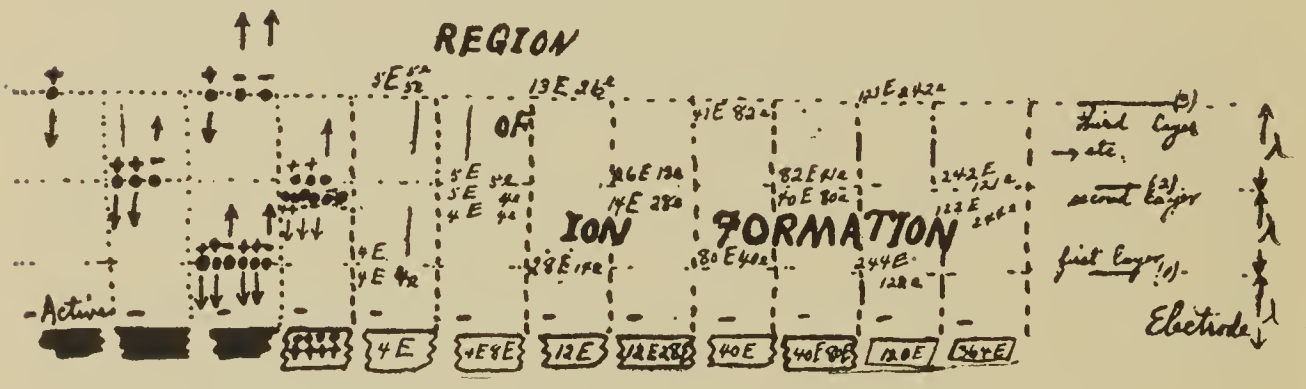
(1) The corona is usually assumed to start from the natural ionization of the gas. The electric field may ionize a gas itself under certain conditions. Fig. 3 shows how ions are easily formed when there is a sufficiently intense electric field acting over a depth of three or more mean free paths. In the figure the mean free path of an ion and a molecule is assumed to be the same, and given the value in air at 76 cm. pressure and 0° C. The length of time between collisions is thus 1/4,600,000,000 second. If this period T is magnified to 1 sec., the period of a 60-cycle current would correspond to about three years. It is thus seen that there is equilibrium between ionization and field as regards the starting of the corona, because the question of a few T time intervals can be neglected.

The natural ionization of a gas which accounts for the lag effects in point discharges would probably produce a lag effect

in the corona discharge. So far no investigations have been made along this line.

(2) The condition of ionization equilibrium is determined by the state existing when the space charge due to the moving ions lowers the electric field so that the rate of formation becomes uniform. This condition should not be confused with the con-

Active Electrode Sections.



Time	0 T	2 T	3 T	4 T	5 T	6 T	7 T	8 T	9 T	10 T
Current Flow to Active Electrode	0	0	0	4E	4E	12E	12E	40E	40E	120E
Through First Layer	0	0	6	6	18	18	60	60	180	180
Through Second Layer	0	3	3	12	12	39	39	120	120	363
Through Third Layer	1	1	4	4	19	19	58	58	181	181
Space Charge—										
Through First Layer	1E	0	12	0	5e	0	13e	0	41e	0
Through Second Layer	0	1E	0	1e	0	1E	0	1E	0	1E
Through Third Layer	0	0	2E	0	4E	0	14E	0	40E	0

E represents a unit + charge.
e represents a unit — charge.

ITEMS.

A space charge that is fluctuating.
A double layer.
The fluctuations of an electrical current in a gas.
An explanation of how a corona starts.
T = 1/4,600,000,000 sec. ¼ cycle (*i. e.* time for e. m. f. to go from 0 to max.) = 1/240 sec.
If T = 1 sec. ¼ cycle = ¾ year.

FIG. 3.

dition of chemical equilibrium, which is very important in the case of the corona discharge in air. Ozone, hydrogen peroxid, oxides of nitrogen, and possibly other compounds modify the corona discharge, and hence the corona discharge may keep on changing while the quantities of these compounds are changing.

(3) Fig. 3 shows how one ion starting at time $T = 0$, produces 2 ions at time $T = 1$, and the action of these ions results in 9 ions being in the gas at a time $T = 3$. In the present case we have

neglected ion recombination and diffusion. The figure shows very clearly how at any time the current through various cross sections of the gas varies, and how the current through the same cross section varies with the time.

(4) Fig. 3 shows how the moving ions act as a space charge. In the case of the rapidly moving gas ions the space charge does not injure precipitation. It can be shown that the fume ions may be the source of a space charge that will choke back the corona current. The figure shows how the space charge fluctuates at any point.

Fig. 4 is made to illustrate the small part that fumes play in the corona discharge. A mean free path cube (λ cube) is one for which the length is that of the path of an ion between collisions and represents the size of a very small fume particle. Each of these cubes contains 27,000 molecules. In dense smoke there is not more than one smoke particle per 20,000,000 of these cubes. Possibly a better picture of the relative size of these particles is this:

an electron—a pin head.

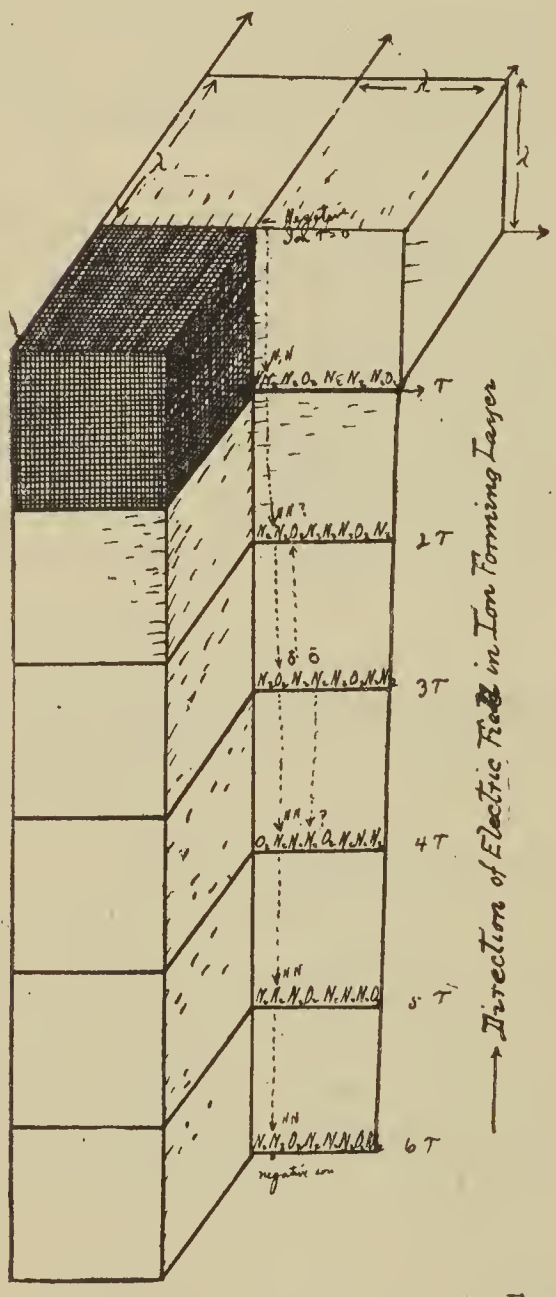
a molecule—the Engineers' Building in New York City.

a mean free path cube—about 30 Pennsylvania railroad stations packed in a cube.

a small fume or smoke particle—Manhattan Island.

The question is frequently asked as to how theory aids in the application of the electrical method to precipitating fumes, dust, smoke, mists, fogs, etc., from gases, the idea prevailing that the operation is extremely simple. The latter view is entirely incorrect, and the illusion is usually dispelled when a treater is to be kept in continuous operation. In short the accurate knowledge of the phenomena involved in precipitation is useful (*a*) in improving the apparatus; (*b*) in making present operation more effective in every way; (*c*) in accurately comparing the various methods of removing suspended matter from gases, and (*d*) in opening new fields for technical operation. The possibilities of improvement in the process are very great and the next few years will see even greater advances than in the past. This can be the more readily admitted when it is remembered that the present technical plants have only been out of the laboratory for a few years.

In present operations of electrical precipitation the value of a thorough knowledge of the process is just as necessary as in the running of an automobile, an aeroplane or any other piece of apparatus. A partial knowledge of a subject may be sufficient for most cases, but circumstances invariably arise that require



IONIZATION
and
Chemical Changes
in the
Electrical Precipitation Process

λ = mean free path of ion and molecule. Both of same order of size.

Volume of each large cube = λ^3.

= 1 cm.

1,000,000,000,000,000 large cubes in 1 cu. cm.

Each small cube contains 1 molecule.

Each large cube contains about 27,000 molecules.

A small cigarette smoke particle is about as large as a large cube λ^3. A dense smoke contains 50,000,000 particles per cu. cm. or one smoke particle per 20,000,000 λ^3 cubes.

FIG. 4.

technical and perhaps even theoretical skill. It is too easily forgotten, too, that the theoretical knowledge of today becomes the technical skill of tomorrow. A resumé of these problems will be made in a later communication. A full knowledge of the precipitation of suspended matter from gases is necessary for the proper comparison of the centrifuge, the settling, the washing, the electrical and other processes used for cleaning gases. The fixa-

tion of nitrogen, the formation of ozone, the disinfection of gases, the differential separation of different materials from gases and the conservation of the heat in gases, are among the many wider applications of the electrical process.

The theory of the corona discharge (with further experiments to make it apply to each type of smoke, dust, fume, mist or fog that constitutes a commercial problem) permits determination of—

(1) The exact calculation of the paths of the fume ions in a treater.

(2) The life of the fume ions and the time required to precipitate them.

(3) The evaluation of the precipitation constant.

(4) The effect of space charges.

(5) The amount of energy flowing into the treater that is actually expended in the precipitation of the fumes.

(6) The maximum velocity of the fumes for complete precipitation.

(7) The calculation of the best size and type of electrodes for a given type of fume.

(8) The best process to apply when it is found difficult to ionize fume particles.

(9) The smallest sized treater necessary to clean a given volume of fume in a given time.

(10) The separation of particles of a substance when a part of a mixture.

(11) The separation from each other of substances that possess different volatilities.

(12) The effecting of chemical reactions such as the fixation of nitrogen, the oxidation of various substances, etc.

(13) Probably the most important application is that of giving a perfect knowledge of the subject in place of a hit-and-miss, vague guessing and surmising state of knowledge that leads laymen to suspect the engineers connected with the work. This psychological effect has played a very important rôle in the past and will be important in the future.

Some of these items have been treated in previous papers, some in the present one, and a complete treatment of the whole subject is being prepared.

THE LIFE AND TRACKS OF FUME IONS.

The fumes enter the precipitator pipe at a density of n particles per cu. cm. These particles become ionized to fume ions and are driven to the pipe by the electric field. The time thus required to precipitate a fume ion will be defined as the life of a fume ion and the path it traverses as the track of the fume ion. The longitudinal velocity of the fumes through the pipe does not affect the life of the fume ion excepting as they may cause a modification in its charge, but it changes the tracks of the fume ions very greatly.

Consider a pipe treater with a corona of radius r_c, pipe of radius R and a cylindrical shell of radius r and thickness dr within the treater. The fume particles become fume ions gradually, but for complete precipitation all the particles become ions. The fume particles $2\ \pi\ n\ r\ dr$ in a unit length of shell eventually become fume ions, each traversing a distance $R - r$ to reach the pipe.

The total distance traversed by all the fume ions of this unit section before precipitation is,

$$\int_{r\ =\ R}^{r\ =\ r_c} 2\ \pi\ n\ r\ dr\ (R - r) \qquad (1)$$

The number of fume particles is

$$\pi\ n\ (R^2 - r_c^2) \qquad (2)$$

(1) divided by (2) gives the average length of track of the fume ion as projected on the r axis,

$$\frac{\frac{1}{3}\ R^3 - Rr_c^2 + \frac{2}{3}\ r_c^3}{R^2 - r_c^2} \qquad (3)$$

In precipitation work $R = 30\ r_c$ approximately, (3) becomes 0.3330 R.

The velocity Vr of a fume ion along the radius is the product of the electric field intensity by the mobility K,

$$v_r = E_v\ K = k\ \frac{Ep}{r\ log_e \frac{R}{r_c}} \qquad (6)$$

where e is the base of the natural system of logarithms.

The fume ions will be carried longitudinally along the pipe by the fume gases with a velocity v_l in the y direction. One has the velocities

$$\frac{dr}{dt} = v_r, \quad \frac{dy}{dt} = v_l \tag{7}$$

$$\int r\, dr = \int \frac{Ep\ k}{\log_e \frac{R}{r_c}}\, dt, \quad \int dy = \int v_l\ dt \tag{8}$$

In the simplest conditions where the constants of integration disappear,

$$\tfrac{1}{2}\ r^2 - \tfrac{1}{2}\ r_c^2 = \frac{Ep\ k}{v_c \log_e \frac{R}{r_c}}\, y. \tag{9}$$

This is the general equation giving the track of the fume ion in a gas.

Let V be the potential difference applied across the electrodes, E_r the potential gradient at any point r cm. from the center, E the voltage drop between the corona and wire and Ep the remainder of the voltage drop, the driving potential that precipitates the fume ions to the pipe.

$$E_p + E_c = V \tag{4}$$

The potential gradient at any point neglecting space charges would be (where a is the radius of the wire),

$$E_r = \frac{V}{r \log_e \frac{R}{a}} \tag{5}$$

The effect of space charges upon the value of the potential gradient will be treated in a later paper. It seems quite certain that any choking of the corona current by space charges is due to ions possessing a mobility of less than 0.1 cm. per sec.

$$P = \frac{Ep\ k}{v_e \log_e \frac{R}{r_c}} \tag{10}$$

is the *precipitation constant, the most important factor to be considered in the precipitation process.* The following table gives the value of P for various sized pipes for $K = 0.001$ and V_e a value of 5 ft. (150 cm.) per sec.

The Precipitation Constant.

	6 in. (15 cm.) Pipe	9 in. (23 cm.) Pipe	15 in. (38 cm.) Pipe
25° C.	0.57	0.85	1.42
400° C.	0.25	0.37	0.63

The application of the above equations will be taken up in detail in a paper to follow the present one.

CONCLUSIONS.

1. The term "corona discharge" has been defined as the luminous and ionizing electrical discharge taking place from the wire electrodes of an electrical precipitation treater. The term "point discharge" need not be used in precipitation work. The term "brush discharge" may be applied to the fan-like parts of the corona discharge as it appears under certain conditions.

2. The two different "regions" of the corona discharge as regards precipitating action and space charges has been described. It has been shown how important it is to keep the fumes to be precipitated within the "region of passive electrode precipitation."

3. The space-charge effects of the small ions of the corona are described. The fact that these space charges do not interfere with electrical precipitation shows that any choking of corona currents by space charges must be due to the large ions.

4. It has been shown how whirls and eddies can exist in the corona discharge and how it may be possible for eddies to exist that possess different senses of rotation. It may be that through the action of eddies of this kind fume particles may be carried within the ion-forming layer.

5. The description of the ionization process in precipitation treaters indicates how easily the deposit of a layer of insulating

material about the active electrode may result in the piling up of space charges in this region and then sparking.

6. The greater the space charge in a treater the less the voltage that can be impressed upon the treater. This follows from the fact that the field of the space charge is in the same direction as that of the treater electrodes, and passes generally through the ionizing layer. Theoretically, the ideal condition would be $R/r_c = e$. Practically this usually exceeds 30, due to the action of space charges.

7. On account of lack of time, the life and tracks of fume ions, the theory of the corona and the application of the precipitation constant have only been touched. Subsequent papers will treat these subjects fully. A proper treatment of this kind makes precipitation engineering an exact science and puts the whole subject on a mathematical basis. The life of a fume ion is usually less than the quarter period of an alternating current cycle.

8. An indication is given as to how the charging of fumes can be made more efficient.

9. The great advances in fume precipitation in the future will be made as regards

(*a*) The more efficient charging of the suspended particles.

(*b*) The maintenance of the corona more continuously and uniformly at its maximum value.

(*c*) The useful applications of the chemical power of the corona as well as its precipitating power.

The present paper is one of a series in which the preceding numbers are as follows: I. The scientific classification of smoke, Rauch and Staub, Dec., 1911; II. The precipitation of smoke, dust and fumes by electricity, Rauch and Staub, June, 1912; the electrical precipitation of suspended matter in gases, Journ. Franklin Institute, Sept., 1912; III. The positive and negative corona, A. I. E. E., June, 1913; IV. Theory of the removal of suspended matter from gases, Journ. Ind. and Eng. Chemistry, Oct., 1913; V. Electrical precipitation, Journal of Engineers' Society, Harrisburg, 1914, etc.; VI. Smoke monitor, London Elec-

trician, June 5, 1914, etc.; VII. Theory of the removal of suspended matter from fluids, A. I. E. E., Feb., 1915; VIII. Elektrische Fällung, Ann. d. Phys., Oct., 1915.

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